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DEVELOPMENT AND EVALUATION OF ANALYTICAL METHODS FOR THE DETERMINATION OF TRACE POLYMERS IN COAL AND OIL PROCESS WATERS

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Final Report

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for

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DEVELOPMENT AND EVALUATION OF ANALYTICAL METHODS FOR THE DETERMINATION OF RESIDUAL POLYACRYLAMIDE POLYMERS IN COAL AND OIL PROCESS WATERS

SUMMARY

This report presents and discusses the results of CANMET/CRL research work on the "Development and Evaluation of Analytical Methods for the Determination of Residual Polyacrylamide Polymers in Coal and Oil Process Waters" (DSS File No. 06SQ.23440-6-9215). The work was carried out by Guelph Chemical Laboratories, a 100 % Canadian company dedicated to energy research and analytical services.

The objective of the study is related to the improvement of the quality of coal, oil and other industrial process waters for reuse or disposal. In this study, an economical, rapid and routinely applicable spectrophotometric methods have been developed for the analysis of cationic, anionic, and non-ionic polyacrylamide polymers in coal and oil process waters. The method development studies include: Starch-triiodide method, Ultra Violet method and Leuco crystal violet method. The feasibility of their application and optimumization to real coal and oil process water samples have been made. PAMs were characterized by elemental analysis (C, H, N, O). As part of the method development studies, spiking and recovery studies were carried out at various concentrations of PAM and absorbance measurements were optimized.

All three methods studied were modified and optimized for sensitiivity in terms of the following parameters: pH, effect of reagents, chlorides as NaCl, iodide as KI, metals such as Ca, Mg, Zn, Al, Fe, and effect of organics likely to be present in process waters and, therefore, causing interferences in the PAM determination.

The application of the developed methods was tested on real samples supplied by CANMET. The results indicate that the newly developed Leuco crystal violet method emerged as the best in terms of simplicity as well as being economical and routinely applicable in the field or laboratory set-up. The method has sufficient novelty and utility to warrent its protection by patent.

The Plan of This Report

The form of presentation of this report involves four parts labelled with Roman Numerals I to IV.

Part I deals with Triiodide method, Part II with Starch Triiodide method, Part III with Leuco Crystal Violet method and Part IV deals with the application and comparison of the various developed methods.

Each part has a section on Introduction, Experimental Approaches, Results and Discussion. Four manuscripts comprising one of each part being written for publication.

PART I

The Triiodide Method

INTRODUCTION

Tailings from coal washery and heavy oil/bitumen processing plants are often discharged to thickeners and then to tailing ponds. In order to achieve sufficient clarity of the water from the settling ponds for either subsequent reuse of discharge to streams, flocculants such as polyacrylamides are usually added as settling aids.[1, 2, 3, 4] Because of environmental constraints, e.g. water conservation, limited land for disposal and general stream pollution, the major portions of process water requirements are now reclaimed from tailings thickeners/tailings ponds. Residual flocculants in the reclaimed waters could affect processing operations, e.g. flotation of coal fines. Therefore, there is a need to develop an analytical technique for monitoring traces of residual flocculant in these reclaimed waters. In addition, monitoring the treated effluent for residual PAM is also necessary prior to discharge into streams.

Qualitative determination of PAM is normally achieved by adding a non-solvent to precipitate the polymer and observing the appearance of a haze. The quantitative determination of polymer is determined in a similar manner except that an instrument is used to measure the turbidity.[2] For example, Vreugde and Poling [5] have determined extremely low residual PAM concentration in supernatant water by making use of the principle that polyanions react with fatty catons or cationic

polyelectolytes to produce insoluble complexes, and then measuring the resultant turbidities by light scattering technique. Attia and Rubio [6] have used tannic acid to precipitate PAM and measured the turbidity by nephelometer. Unfortunately, the formation and measurement of precipitates in the above turbidometric procedure are influenced by a number of variables which usually have an effect on the particle size or the solubility of the polymer. The molecular weight distribution of the polymer, the rate of addition of precipitant, the order and the time of mixing, and the presence of residual dissolved organics in process waters are known to cause variation in the measured turbidity and result in erratic responses.

A starch-triiodide method was used by Scoggins and Miller[7] for the determination of water-soluble polymers containing primary amide groups. Although the study appeared promising, a number of problems were encountered. Factors that interferred with the determination most are: the pH of the solution, halides, oxididants, and organics. The effect organics studied in reference 7 does not include humic and falbic acid impurities and the method was not optimized for using to coal wash waters. Further more, the ionic strength of the medium was not kept constant.

A spectrophotometric method in the UV range at 287 nm for the determination of PAM in water has been described in the

manufacturer bulletin.[8] However, as is expected, interferences from other materials heavily absorbing in the vicinity of 287 nm are found to have been interfering and, therefore, this method in its present form cannot be applied for the determination of PAM to coal and oil processed water.

From the foregoing, it would then appear that there is a need for a development and evaluation of method for the determination of trace polyacrylamide polymer in coal and oil processed water. In part I and part II of this study modified triiodide and starch triiodide methods are examined. In part III, Leuco crystal violet method for PAM determination which is simple, sensitive and economical can be adapted in field or laboratory set-up is developed. In this method, iodide is oxidized to iodine by N-bromo amide polymer (PAM-Br) produced by bromination of PAM. The iodine that is produced reacts instantaneously with colourless Leuco Crystal violet, 4, 4', 4''-methylidynetris (N,N-dimethylaniline) to produce intense blue colour. The developed colour is stable and obeys Beer's law over range of PAM concentration in excess of iodide ion. The mechanism of the triiodide method involves the bromination of the amide groups on PAM to N-bromoamide:

$$RCONH_2 + Br_2 \longrightarrow RCON\begin{matrix}H\\Br\end{matrix} + HBr$$

The N-Bromoamide in water is in equilibrium with hypobromous acid and PAM:

$$RCON\begin{matrix}H\\<\\Br\end{matrix} + HOH = RCONH_2 + BrOH$$

The excess bromine from the initial reaction is destroyed with sodium formate:

$$Br_2 + HCOONa \longrightarrow Na^+ + 2Br^- + CO_2$$

The hypobromous acid formed in the second equilibrium oxidises iodide to iodine:

$$BrOH + I^- + 2H^+ \longrightarrow (1/2)\ I_2 + HBr + HOH$$

Iodine is converted to triiodide with excess iodide:

$$I_2 + I^- \longrightarrow I_3^-$$

and the triiodide is read spectrophotometrically in the ultraviolet range at a wavelength of 287 nm.

Based on this mechanism, it follows that contaminants of an oxidising nature have the potential to produce high results due to oxidation of iodide to iodine. This includes any excess bromine which is not completely destroyed by sodium formate. Typical coal water contaminants also have the potential to produce high results due to their direct absorption in the ultraviolet range. Several organic,

cationic and anionic contaminants were introduced to the triiodide method to test the feasibility of applying the method to coal water samples without elaborate filtration or purification techniques.

EXPERIMENTAL

Reagents and Apparatus

Anionic Dow Separan MG 700 was used as standard polyacrylamide (PAM). Stock solutions were prepared by accurately weighing 70 to 80 mg of PAM into a 500 ml volumetric flask and wetting the polymer with 1 ml of methanol before diluting to volume with distilled water. A 100 ml aliquot of the stock solution was diluted to 250 ml for the standard 55 to 66 ppm PAM solution. The actual PAM concentration was calculated by accounting for the percent moisture in the PAM. Both stock and standard PAM solutions were shaken or stirred for at least 3 hours prior to use. Stock solutions were stable for more than 6 months where as standards would loose strength in one to two weeks.

The buffer solution was prepared to maintain a pH of 4.3. 50 g of anhydrous sodium acetate was dissolved in 83 ml of glacial acetic acid and diluted to 1000 ml with distilled water. The pH was adjusted to 4.2 with 50 % acetic acid.

Other reagents included; a 500 g/l sodium formate solution, saturated bromine water (prepared fresh daily) and a 150 g/l potassium iodide solution which was discarded when it turned yellow. All the reagents were used to determine the sensitivity of the optimum method and study the effect of interferences. Variations of the reagent amounts were used to develop the final optimum method.

Absorbance measurements were made on a Beckman Acta III Spectrophotometer at a wavelength of 287 nm in 1 cm quartz cells. Elemental analysis of the PAM standard polymer was performed on a Perkin-Elmer Model 240 Elemental Analyser and a Varian Techtron Atomic Absorption Spectrophotometer.

Procedure

Determination of a standard curve was accomplished by preparing aliquots from 0.2 to 10 ml of standard PAM solution in 50 ml graduated test tubes. The solutions were diluted to 35 ml with distilled water and reagents were introduced with shaking after each addition. The standards were brominated with 1 ml of saturated bromine water then were allowed to sit for 10 minutes. Excess bromine was destroyed with 0.2 ml of sodium formate solution and the solutions were left to sit another 10 minutes before 1 ml of potassium iodide was added. Each standard was read spectrophotometrically after 2 minutes and within 10 minutes at a wavelength of 287 nm in 1 cm quartz cells with a distilled water reference. A standard curve of absorbance versus ug of PAM was plotted from the resulting data.

The optimum conditions for the method were derived by adapting the procedure to standards of constant PAM mass (usually 250 ug) and varied aliquots of the reagents. Applying this to potassium iodide was straight forward.

However, determination of the optimum pH required new buffers for each point in the acidic range and pH adjustments for points in the basic range. At the point in the procedure reserved for buffer addition, aliquots of 0.2 N sodium acetate and aliquots of various concentrations of acetic acid from 0.2 N to glacial were added. This maintained a range of pH values below pH 5. 1 N and 30 % NaOH were used to acquire higher pH values, however pH monitoring and adjustments were required after the addition of each reagent in order to maintain the pH, especially after bromination.

Contaminants were initially examined for the magnitude of their absorbance at the 287 nm wavelength. Contaminants without absorption were further examined for their effect on the method. Aliquots of a solution of contaminant were added to a series of PAM standards of equal mass (usually 250 ug PAM). Reagents were added according to the general procedure and then plots of absorbance versus compound or ion mass were produced. These experiments were repeated under constant ionic strength conditions by adding 5 ml of a 100 g/l solution of sodium sulphate to the samples before reagent addition. Those interferences with a positive effect on colour intensity were studied in the absence of PAM. From these experiments, the nature of the interferences, if any, were determined for a particular compound or ion.

DISCUSSION AND RESULTS

Experiments were designed to derive the method conditions that would provide optimum results and to examine the effects on the method of contaminants typically found in coal wash waters. Parameters considered in the optimisation of the method were linearity, sensitivity and stability of the developed colour. Various coal water contaminants where studied to determine the nature, cause and mass range of their effects on the method.

Results of analysis on DOW Separan MG 700 polymer are summarized in Table 1. Due to the availability of amide groups for bromination, the percentage of acrylamide groups on the polymer was proportional to colour development in the triiodide method. Details of the method for acrylamide group determination are in Appendix 1 at the end of this series.

TABLE 1

ANALYSIS OF DOW SEPARAN MG 700

Carbon	41.07 % of dry mass
Hydrogen	5.37 % of dry mass
Nitrogen	11.04 % of dry mass
Sodium	12.18 % of dry mass
Oxygen	29.89 % of dry mass
Ash	24.6 % of dry mass
Acrylamide Groups	49.0 % of dry mass
Moisture	13.1 % of total mass

Optimisation of the Method

Acidic conditions for the triiodide method provided optimum sensitivity and easy application. Maximum absorbance values and minimum blank values, under constant PAM conditions, were achieved in a pH range from 3.5 to 4.5 (Fig. 1). Values of pH in this range were easily maintained throughout the method with acetate buffer.

High absorbances were also observed at pH values greater than 7, but a basic medium proved impractical for the method. Maintainance of high pH required pH adjustments throughout the procedure due to HBr formation after PAM bromination and destruction of excess bromine by sodium formate. Even the highest capacity alkaline buffers could not maintain alkalinity after polyacrylamide bromination. Also, alkalinity itself consumed bromine by pulling the following equilibriums to the right (9):

$$2Br_2 + 2HOH = 4H^+ + 4Br^- + O_2$$

$$Br_2 + HOH = H^+ + Br^- + HOBr$$

Acidic conditions were applied to the method more effectively.

Colour intensity increased proportionally with the amount of potassium iodide reagent added (Fig. 2). However, more than 150 mg of KI induced high blanks. Therefore, the conditions outlined in the procedure were the ultimate compromise between maximum colour development and minimal interference

from the reagents.

The optimum reaction times for the bromination of PAM reduction of excess bromine and development of colour were adopted from other procedures and also derived experimentally. Scoggins (7) found that a 15 to 40 minute bromination period and a five minute reduction time produced maximum absorbance values for PAM determination by the starch-triiodide method. Nevertheless, reaction times suggested by the Dow Chemical Company (8) were applied to the method. The ideal time for colour development after the addition of potassium iodide was determined to be between 2 and 10 min (Fig. 3). Colour intensity for PAM standards less than 115 ug remained unchanged after 30 minutes of colour development but there was noticeable deterioration in colour for PAM standards greater than 210 ug. Despite a 35 % drop in absorbance values after 5 hours, absorbances remained linear with respect to PAM concentration. Reaction times applied to the method produced favourable sensitivities.

The triiodide method applied under the optimum conditions was sensitive to 0.3 ug of PAM*, and was linear over 500 ug of PAM. The standard curve (Fig. 4) had a correlation coefficient (r^2) of 1.000 and a blank value of 0.040 absorbance units. Under constant ionic strength conditions,

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* Amount of PAM, in the final volume, required to give an absorbance of 0.001 units when measured in 1 cm cells.

the linearity remained unchanged; however, the sensitivity was compromised with PAM detectable to 0.4 ug.

Ionic Strength

Sodium sulphate was used to study the effect of ionic strength and was found to counteract colour development due to polyacrylamide when present over 0.2 g. Over 3 g of Na_2SO_4 decreased absorbance values by 20 % or more. Absorbance due to more than 5 g of sodium sulphate was revealed in the absence of PAM, however, it was masked by the intense negative influence on polyacrylamide colour development when PAM was present (Fig. 5).

The double charge on sulphate made it useful as an ionic strength buffer, assuming that this was the only factor contributing to its effect on the method. Ionic strength was held constant by introduction of a known excess amount of sodium sulphate into the procedure. Hence, the cause of any interference was attributed to ionic strength if its effects were observed under normal conditions but not under constant ionic strength. The standard curve for the triiodide method under constant ionic strength was less sensitive than under normal conditions, however, it remained linear.

Effect of Divalent Metallic Ions

Divalent calcium was examined in the nitrate form and magnesium, zinc and ferrous iron as their sulphates. The metal sulphates were introduced in quantities low enough for

a negligible effect from sulphate as determined by the ionic strength studies. Magnesium and zinc had no influence on colour development when present below 10 mg. Similarly, less than 1 mg of calcium had no effect on triiodide method results.

Greater than 0.001 mg of ferrous iron caused high absorbances in the absence of PAM. The effect was observed visually in the solutions as an orange-brown colour that appeared after bromination and persisted after the destruction of excess bromine. The colour was characteristic of ferric bromide (10) suggesting the presence of Fe^{3+}. Ferric ion was confirmed by the development of a dark red colour on the addition of potassium thiocyanate indicator to the procedure after the bromine destruction step. Bromine oxidised ferrous ion to ferric ion in a manner similar to the reaction (9):

$$Br_2 + 2FeSO_4 + H_2SO_4 \text{ -------> } Fe_2(SO_4)_3 + 2HBr$$

The ferric ion produced reacted with excess bromine to form the orange-brown colour. The same colour was developed by the direct reaction of ferric ion with bromine.

Effect of Trivalent Metallic Ions

Over 0.001 mg of ferric iron absorbed at the method's wavelength. This occured both with the chloride form of iron which was examined and, to a greater extent, with the bromide form which developed after the bromination step. The effect

was detected visually by an orange-brown colour in solution which was also observed in the examination of ferrous interference.

Absorbances resulting from 210 ug of polyacryamide were enhanced 23 % by the addition of more than 1 mg of trivalent aluminium in the sulphate form (Fig. 6). Colour was intensified with as low as 0.1 mg Al^{3+} in the presence of PAM, however, colour did not develop without PAM. Scoggins (7) observed a similar effect from aluminium with the starch-triiodide method but the magnitude of Scoggins' results were not duplicated when the same range of aluminium masses were studied. No effect was observed with 0.04 mg of aluminium and 200 mg of PAM whereas Scoggins observed absorbances doubling. He attributed the effect to decreased steric hinderance on polyacrylamide during the bromination step due to an interaction of Al^{3+} with the carboxylate groups on the polymer.

Effect of Other Cations

Less than 65 mg of sodium had a negligible influence on the method results as deduced from the study of ionic strength effects with sodium sulphate (Fig. 5). 1000 mg of sodium decreased absorbance by 20 % assuming no influence from sulphate. Since this assumption was drastic, sulphate was held partially accountable and the effect of sodium was dismissed as minimal at levels below 1000 mg of sodium. Any

observed effects from sodium were attributed to ionic strength origins.

More than 1 mg of ammonium ion, in its chloride form, inhibited colour development. The magnitude of chloride's effect did not account for the 73 % drop in the absorbance due to polyacrylamide that was observed with 10 mg of NH_4^+. Therefore, the effect was due to ammonium alone. Depletion of bromine's yellow colour, proportional to ammomium mass, was also observed after bromination of PAM. Restrained colour development was, therefore, due to competition for bromine between NH_4^+ and PAM.

Effect of Anions

Chloride and phosphate were studied as their sodium salts and nitrate in the calcium form. Phosphate and nitrate did not exhibit an effect on the method results when present below 50 mg and 3 mg respectively. More than 600 mg of chloride depleted the absorbance by 25 % of the original absorbance due to polyacrylamide. Constant ionic strength conditions did not alter this result and the influence of sodium in the salt was negligible. The effect was detectable with greater than 6 mg of chloride and the source was other than that of ionic strength.

Greater than 0.05 ug of iodide propagated colour development in the absence of polyacrylamide. Absorbance was linearly proportional to iodide mass with more than 80 ug of I^- (Fig.

7). On reaction with bromine, iodide was capable of both direct oxidation to iodine and formation of iodine dibromide by the mechanism (6):

$$2I^- + Br_2 \longrightarrow 2Br^- + I_2$$

$$I_2 + Br_2 \longrightarrow 2IBr$$

$$IBr + Br^- \longrightarrow IBr_2^-$$

The magnitude of iodide interference depended on the extent to which the mechanism proceeded to completion, and on the potential of iodine dibromide to absorb at the method's wavelength.

Effect of Organic Contaminants

More than 0.05 mg of phenol, 0.8 mg of acetone, 0.1 mg of maleic acid, 0.01 mg of humic acid and small amounts of suspended oil in 25 ml of water at pH 4.2 all had absorbances greater than 0.001 units at the method's wavelength. Maleic acid also caused slow colour development if absorbances were read more than 1 minute after potassium iodide reagent addition (Fig. 8). The rate of colour development was proportional to the mass of maleic acid present.

TABLE 2
EFFECT OF INTERFERENCES ON THE TRIIODIDE METHOD

CONTAMINANT	MIN. AMT. FOR AN EFFECT	EFFECT ON COLOUR INTENSITY	NATURE OF INTERFERENCE	FIGURE #
Sodium Sulphate	200 mg	negative	ionic strength	5
Divalent Calcium	>1 mg	none	--	--
Divalent Magnesium	>10 mg	none	--	--
Divalent Zinc	>10 mg	none	--	--
Ferrous Ion	0.001 mg	positive	ferric bromide abs.	--
Ferric Ion	0.001 mg	positive	ferric bromide abs.	--
Trivalent Aluminium	0.1 mg	positive	colour enhancement	6
Sodium	<1000 mg	negative	ionic strength	5
Ammonium	1 mg	negative	bromine depletion	--
Chloride	6 mg	negative	unknown	--
Phosphate	>50 mg	none	--	--
Nitrate	>3 mg	none	--	--
Iodide	5exp(-5)mg	positive	colour development	7
Phenol	0.05 mg	positive	phenol absorbance	--
Acetone	0.8 mg	positive	acetone absorbance	--
Maleic Acid	0.1 mg	positive	maleic acid absorbance	8
Humic Acid	0.01 mg	positive	humic acid absorbance	--
Oil	--	positive	oil absorbance	--

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PART I

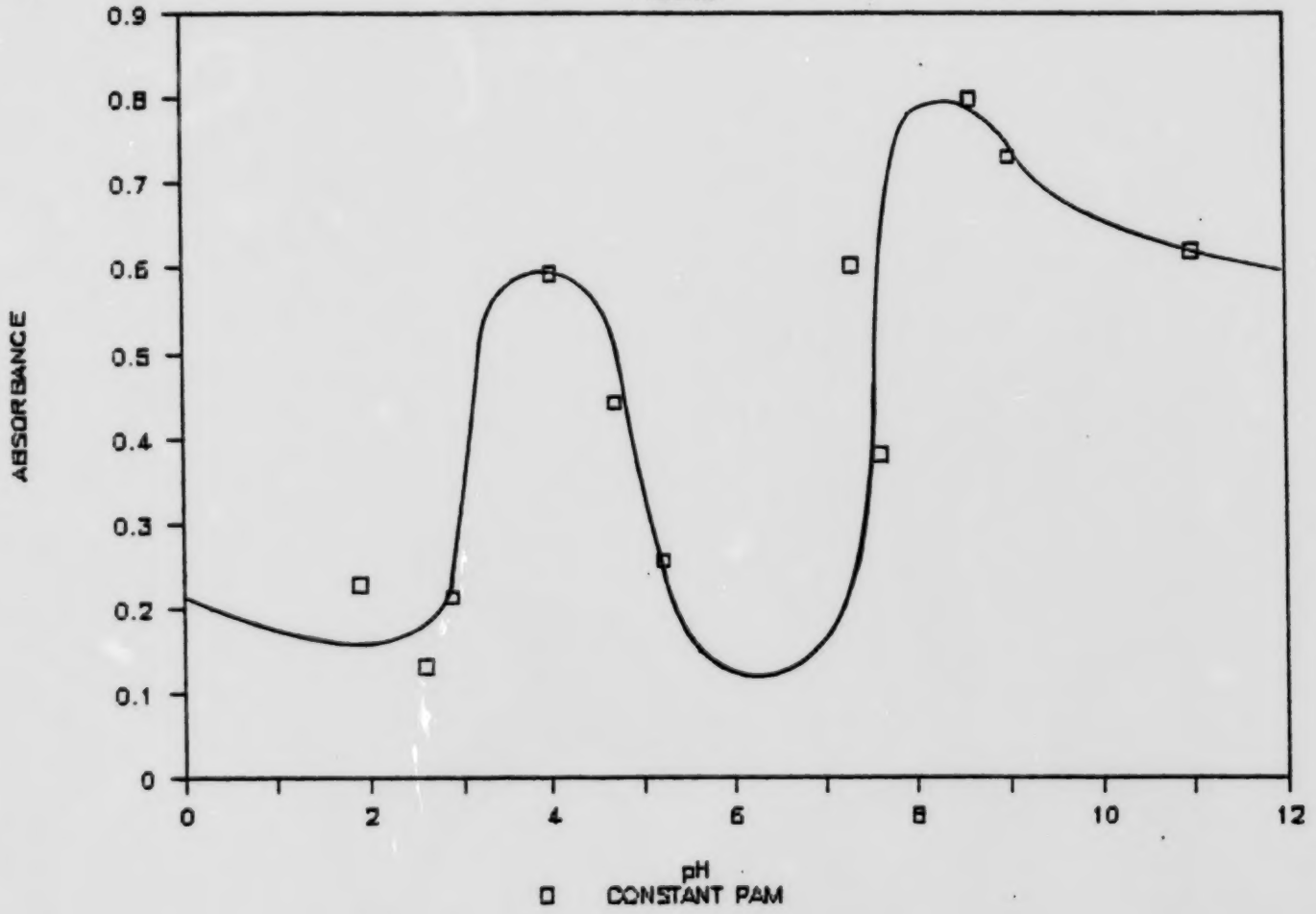
EFFECT OF pH
Figure 1

Final Adjusted pH	Absorbance
1.9	0.229
2.6	0.132
2.9	0.214
4.0	0.593
4.7	0.443
5.2	0.257
7.3	0.604
9.7	2.700
7.6	0.380
8.6	0.800
9.0	0.731
11.0	0.620

Experimental Conditions:
- Experiment #..... DOW 2
- Final Volume..... 37.2 ml
- Mass PAM..... 255 ug
- Path Length..... 1 cm
- Wavelength..... 287 nm

EFFECT OF pH

FIGURE 1



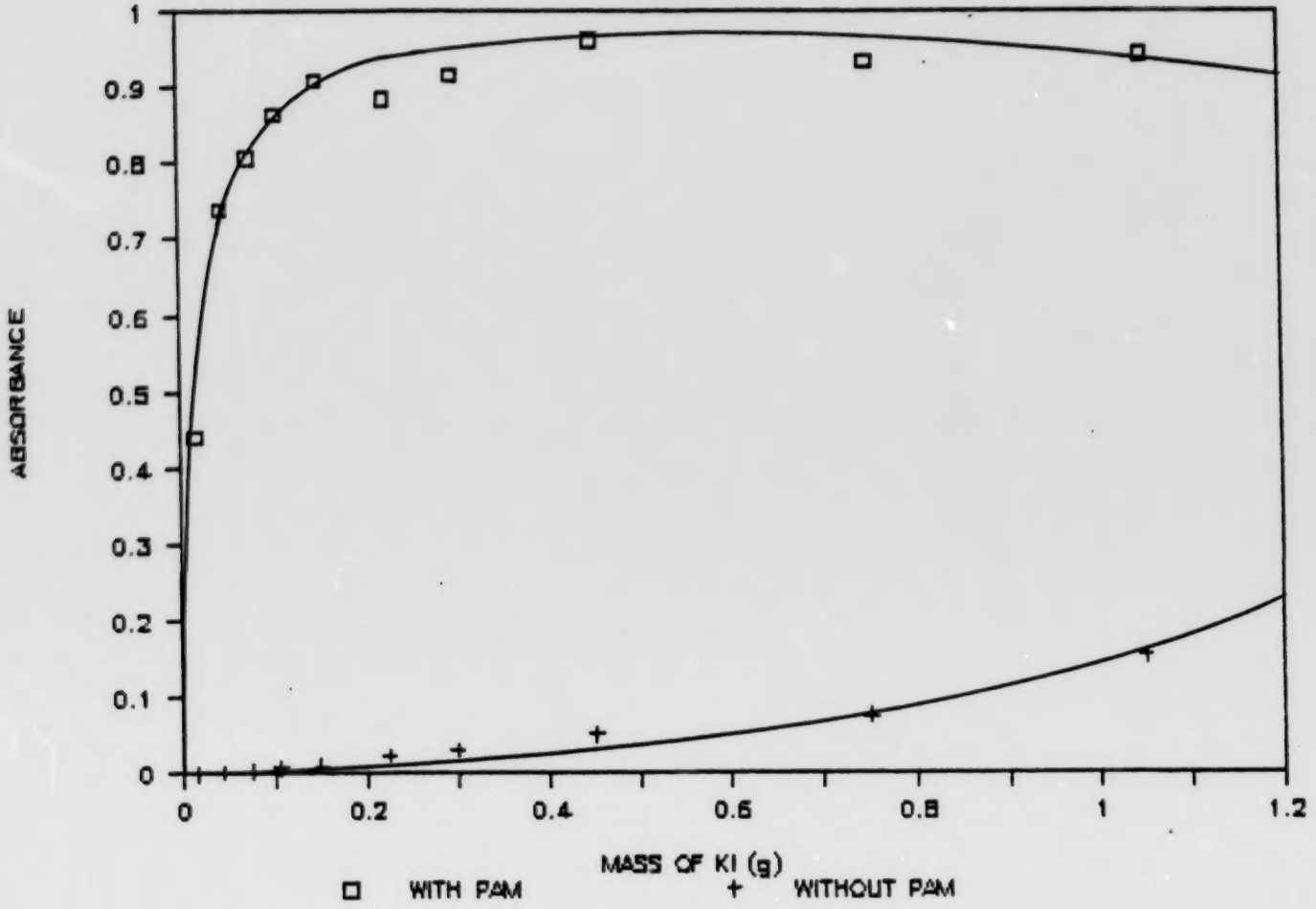
PART I

OPTIMISATION OF POTASSIUM IODIDE REAGENT
Figure 2

Mass of Potassium Iodide (g)	Absorbance	
	With PAM	Without PAM
0.075	0.808	0.002
0.105	0.864	0.007
0.150	0.908	0.010
0.225	0.884	0.023
0.300	0.915	0.031
0.450	0.961	0.051
0.750	0.934	0.076
1.050	0.944	0.155
1.500	0.989	0.115
Experimental Conditions:		
Experiment #	DOW 4	DOW 4
Final Volume	37.2 ml	37.2 ml
Dry Mass PAM	358 ug	0 ug
Path Length	1 cm	1 cm
Wavelength	287 nm	287 nm

OPTIMIZATION OF KI

FIGURE 2



PART I

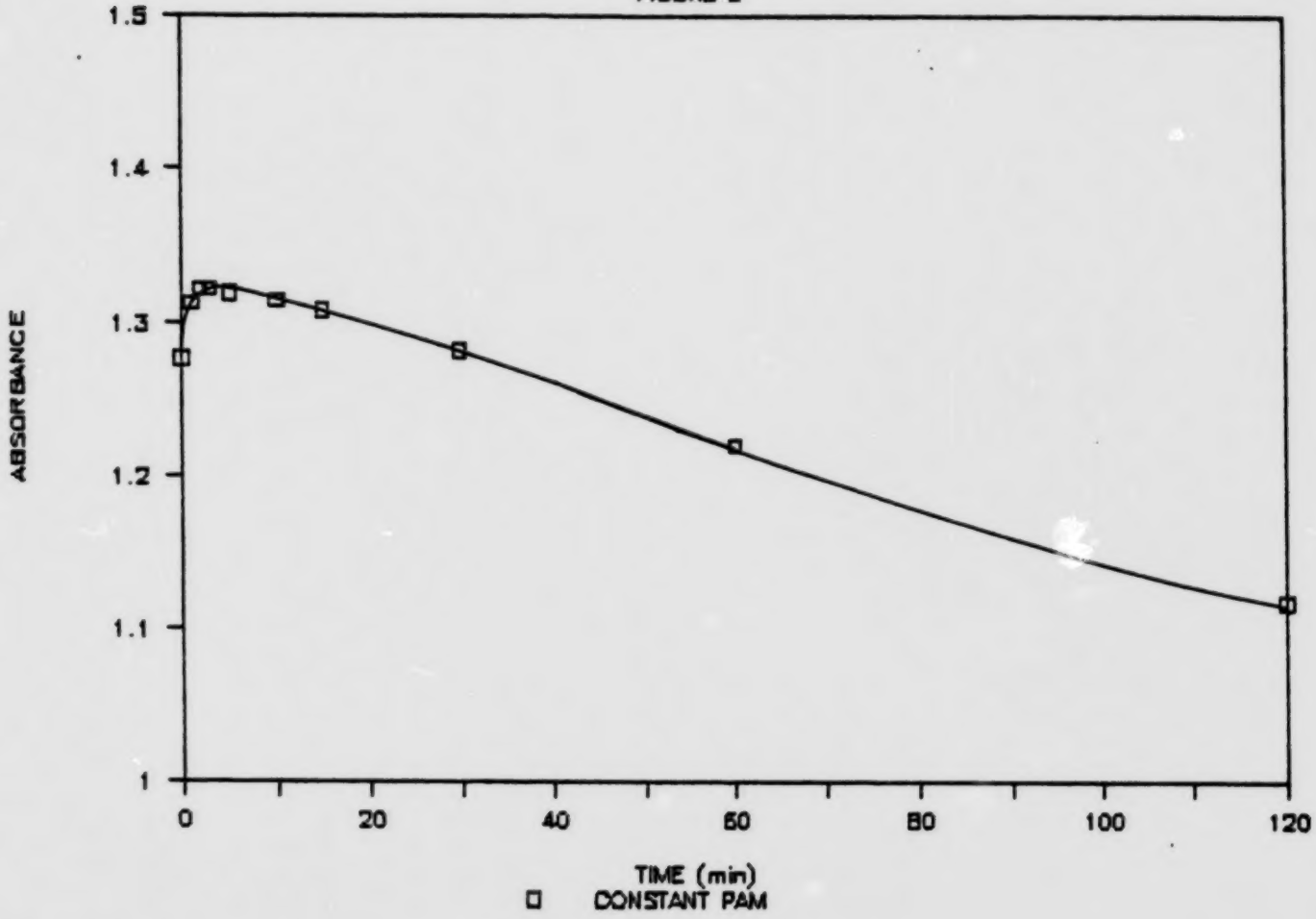
TIME STABILITY OF PAM CURVE
Figure 3

Time (min)	Absorbance
0	1.276
1	1.312
2	1.321
3	1.321
5	1.319
10	1.314
15	1.308
30	1.282
60	1.220
120	1.118

Experimental Conditions:
Experiment #..... DOW 5
Final Volume..... 37.2 ml
Dry Mass PAM..... 358 ug
Path Length..... 1 cm
Wavelength..... 287 nm

TIME STABILITY OF PAM CURVE

FIGURE 3



PART I

PAM CONCENTRATION CURVE
Figure 4

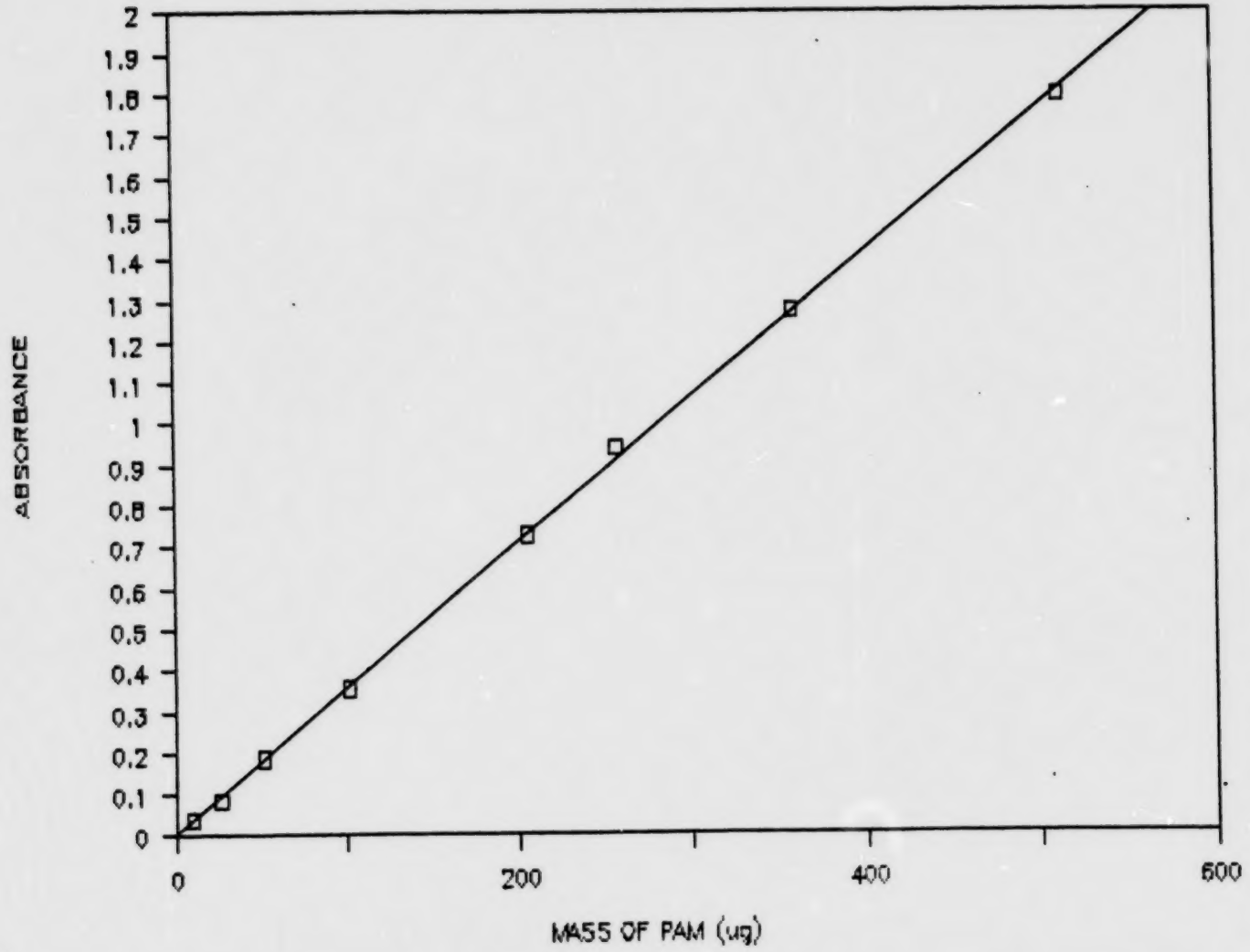
#	Mass of PAM (ug)	Absorbance Minus Intercept
1	0	0.026
2	10.2	0.037
3	25.6	0.084
4	51.1	0.185
5	102.3	0.356
6	204.6	0.728
7	255.8	0.939
8	358.1	1.274
9	511.5	1.798

Experimental Conditions:
- Experiment #..... DOW 5
- Final Volume..... 37.2 ml
- Path Length..... 1 cm
- Wavelength..... 287 nm

Linear Statistics:
- Points Used 2-9
- Intercept..... 0.045
- Correlation Coefficient..... 1.000
- 1/Slope..... 282.9

PAM CONCENTRATION CURVE

FIGURE 4



PART I

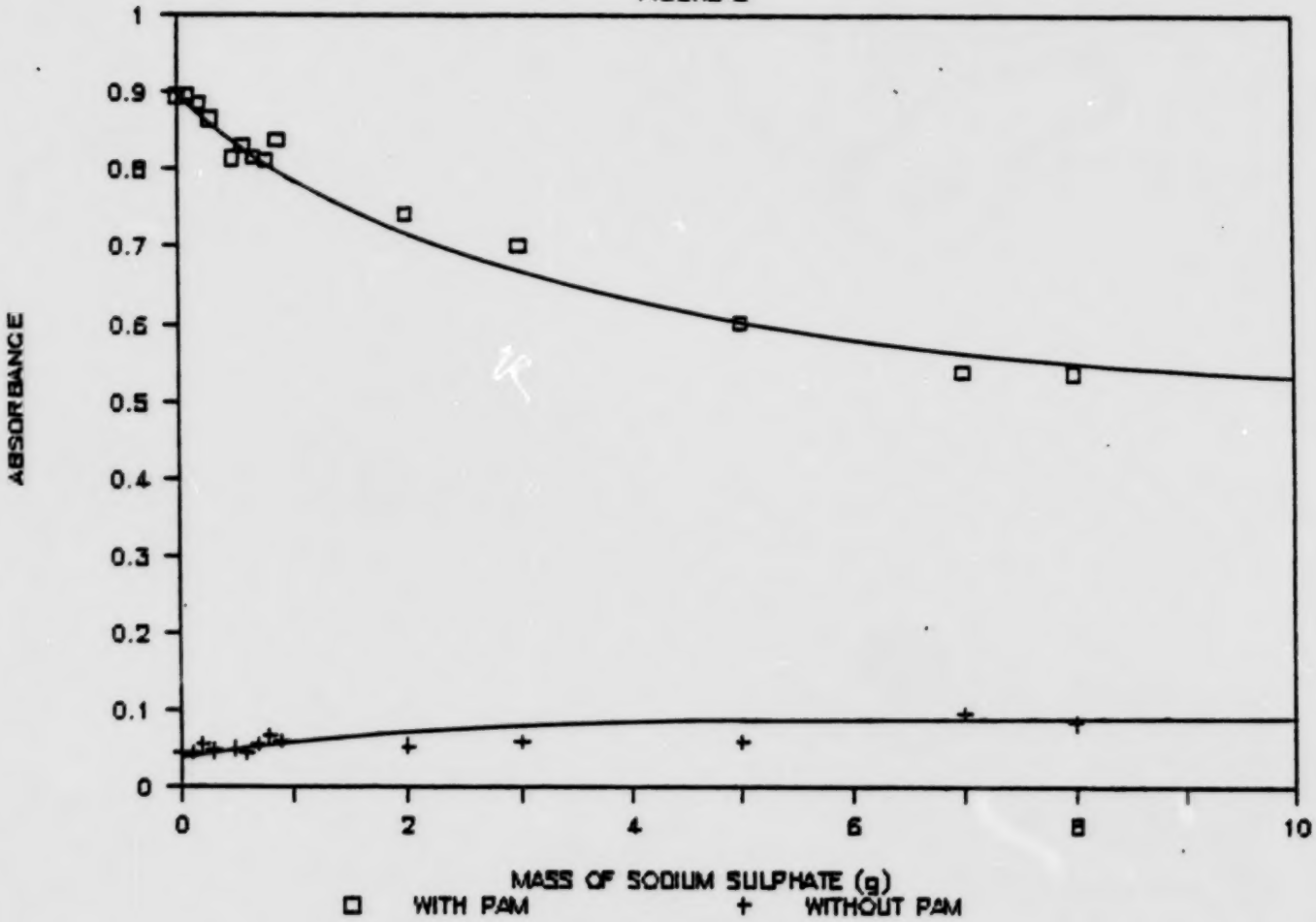
EFFECT OF IONIC STRENGTH
Figure 5

Mass of Sodium Sulphate (g)	Absorbance	
	With PAM	Without PAM
0.0	0.895	0.044
0.1	0.897	0.046
0.2	0.886	0.055
0.3	0.865	0.047
0.5	0.815	0.050
0.6	0.831	0.045
0.7	0.817	0.056
0.8	0.812	0.066
0.9	0.838	0.060
2.0	0.742	0.054
3.0	0.702	0.060
5.0	0.603	0.060
7.0	0.540	0.098
8.0	0.538	0.084

Experimental Conditions:		
Experiment #	DOW 6	DOW 7
Final Volume	37.2 ml	37.2 ml
Dry Mass PAM	255 ug	0 ug
Path Length	1 cm	1 cm
Wavelength	287 nm	287 nm

EFFECT OF IONIC STRENGTH

FIGURE 5



PART I

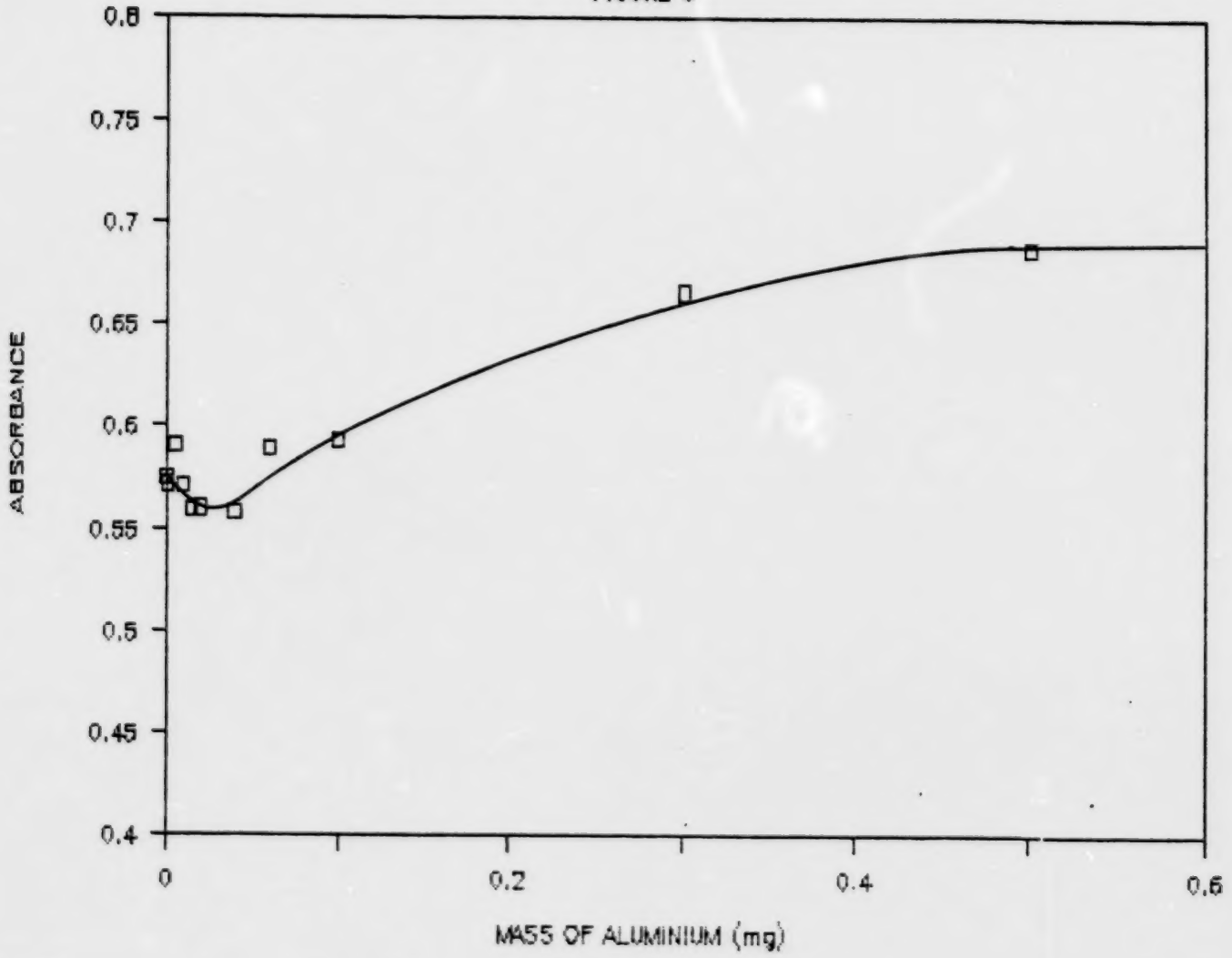
EFFECT OF ALUMINIUM
Figure 6

Mass of Aluminium (mg)	Absorbance
0.000	0.575
0.001	0.572
0.005	0.591
0.010	0.571
0.015	0.559
0.020	0.560
0.040	0.558
0.060	0.590
0.100	0.594
0.300	0.666
0.500	0.688

Experimental Conditions:
- Experiment #..... DOW 22
- Final Volume..... 37.2 ml
- Dry Mass PAM..... 179 ug
- Path Length..... 1 cm
- Wavelength..... 287 nm

EFFECT OF ALUMINIUM

FIGURE 6



PART I

IODIDE EFFECT ; WITHOUT PAM
Figure 7

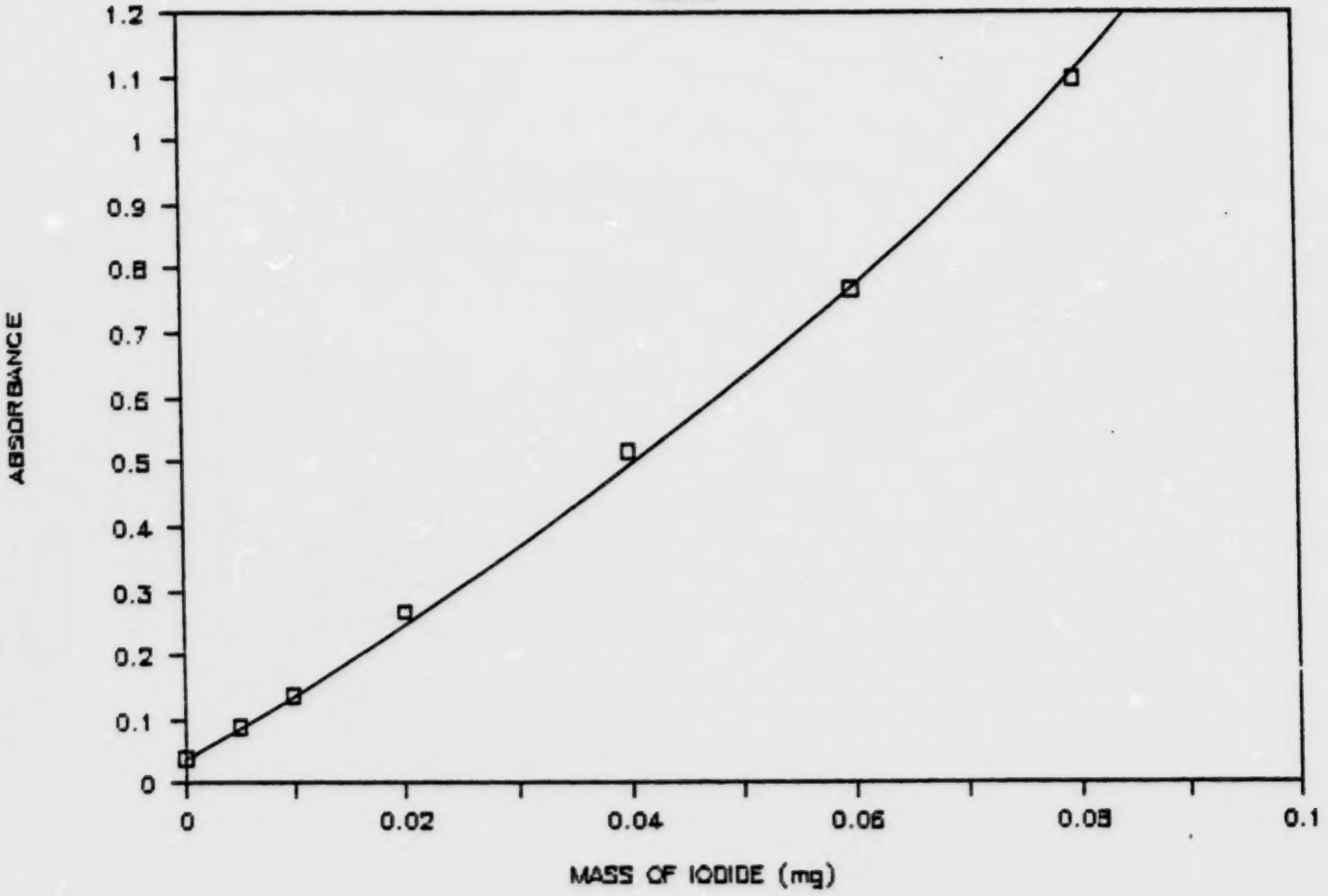
Mass of Iodide (mg)	Absorbance
0.000	0.038
0.005	0.088
0.010	0.136
0.020	0.266
0.040	0.518
0.060	0.768
0.080	1.096

Experimental Conditions:

Experiment #.....	DOW 24
Final Volume.....	37.2 ml
Dry Mass PAM.....	0 ug
Path Length.....	1 cm
Wavelength.....	287 nm

IODIDE EFFECT; WITHOUT PAM

FIGURE 7



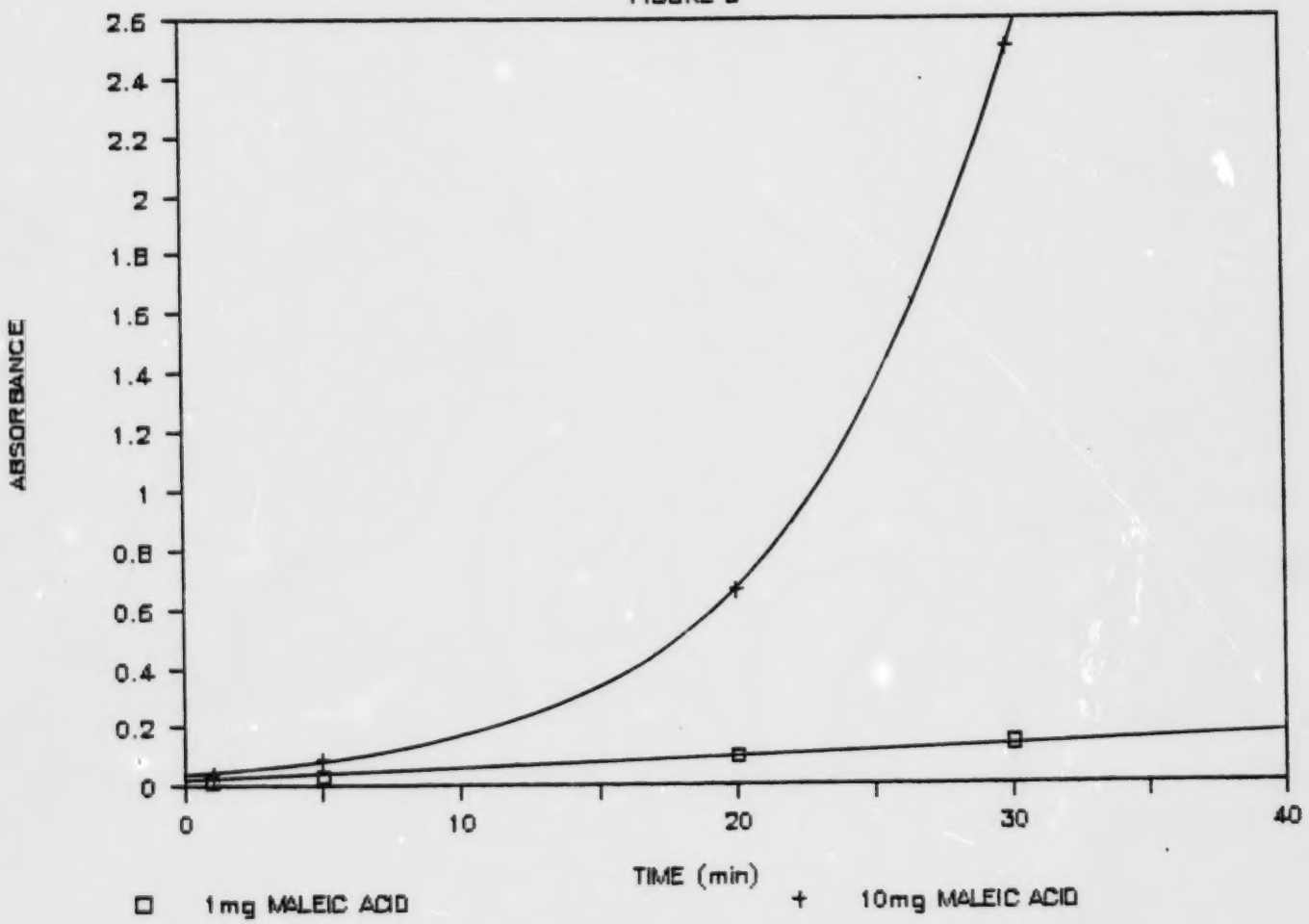
PART I

EFFECT OF MALEIC ACID OVER TIME
Figure 8

Time (min)	Absorbance	
	1 mg Maleic	10 mg Maleic
1	0.017	0.037
5	0.031	0.085
20	0.098	0.660
30	0.140	2.500
Experimental Conditions:		
Experiment #	DOW 20	DOW 20
Final Volume	37.2 ml	37.2 ml
Dry Mass PAM	0 ug	0 ug
Path Length	1 cm	1 cm
Wavelength	287 nm	287 nm

EFFECT OF MALEIC ACID OVER TIME

FIGURE 8



PART II

Starch Triiodide Method

INTRODUCTION

The starch-triiodide method is based on the triiodide method. The mechanism for the development of triiodide from brominated PAM and iodide is the same as described in Part I. However, the triiodide is complexed with a linear starch reagent. The absorbance of the colour of the blue complex is read spectrophotometrically in the visible range rather than in the ultraviolet range. Scoggins successfully developed and optimised the procedure and applied the method to actual coal water samples. However, the effect of contaminants were not studied in detail or under constant ionic strength conditions. As a follow-up on Scoggins' work, several organic, cationic and anionic contaminants were introduced into the starch-triiodide method in order to observe the limits of the interferences as well as their origins.

EXPERIMENTAL

Reagents and Apparatus

Reagents were prepared as described by Scoggins (1) with the exception of the buffer solution which was prepared free of aluminium*. PAM solutions were prepared as described in the triiodide method (2) using Dow Separan MG 700 (an anionic polyacrylamide). The actual PAM concentration was calculated by accounting for the percent moisture in the PAM. The starch-cadmium iodide colour reagent was prepared as described by Lambert (3) using Soluble Potato Starch obtained from J. T. Baker Chemical Co..

Absorbance measurements were made on a Beckman Acta III Spectrophotometer at a wavelength of 610 nm in 1 cm quartz cells. Elemental analysis of the PAM standard polymer was performed on a Perkin-Elmer Model 240 Elemental Analyser and a Varian Techtron Atomic Absorption Spectrophotometer.

Procedure

Initial experiments were performed by adding aliquots from 0 to 10 ml of interference solution to separate 5 ml volumes of PAM solution that were equal in PAM concentration (usually 30 ppm). The reagents were added according to Scoggins' method (1). These experiments were repeated for each interference in the presence of 10 ml of 2.3 M sodium sulphate solution

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* Scoggins used Al^{3+} in the buffer to enhance the reaction of PAM with bromine.

which was added before the interference solution. Excess sodium sulphate acted as an ionic strength buffer, so that the effects of interferences could be studied under constant ionic strength conditions.

Those interferences with a positive effect on colour intensity were further examined in the absence of PAM. This determined whether or not the contaminant oxidised iodide or enhanced the PAM reaction with the reagents.

DISCUSSION AND RESULTS

Preliminary experiments and observations were made to derive conditions for the study of interferences in the starch-triiodide method. Experiments showed that the method was linear up to 260 ug of PAM and sensitive down to 0.5 ug of PAM*, with a correlation coefficient (r^2) of 1.000. The starch-triiodide complex was stable for more than 12 hours, however, all absorbances were read within 1 hour of the colour development in order to maintain consistancy. Concentrated PAM solutions (over 115 ppm) were stable for more than 6 months and diluted PAM solutions, around 30 ppm, were stable one week. Both diluted and stock solutions required shaking or stirring for at least 3 hours prior to use to maintain homogeniety. The optimum pH for the method was in the range from 3.5 to 4.0 (Fig. 1). Scoggins (1) suggested pH 3.5 since chloride interference was non existant below pH 4. Experiments to examine the effect of various interferences were performed keeping in mind all these factors.

Results of analysis on DOW Separan MG 700 polymer are in Table 1. The percentage of amide groups on the polymer was proportional to colour development in the starch-triiodide method due to the availability of amide groups for

---

* Amount of PAM, in the final volume, required to give an absorbance of 0.001 units when measured in 1 cm cells.

bromination. Scoggins (1) applied the method to anionic polyacrylamide standards with amide groups ranging from 23 to 62 percent hydrolysed or in other words standards with 32 to 72 percent acrylamide groups per unit mass. Details of the method for acrylamide group determination and the calculation of percent acrylamide groups per unit weight given the percentage of hydrolysed amide groups, are both in Appendix 1 at the end of this series.

TABLE 1

ANALYSIS OF DOW SEPARAN MG 700

Carbon	41.07 % of dry mass
Hydrogen	5.37 % of dry mass
Nitrogen	11.04 % of dry mass
Sodium	12.18 % of dry mass
Oxygen	29.89 % of dry mass
Ash	24.6 % of dry mass
Acrylamide Groups	49.0 % of dry mass
Moisture	13.1 % of total mass

Effect of Ionic Strength

The effect of ionic strength was studied using sodium sulphate. The overall effect of sodium sulphate on the reaction of PAM with the reagents was negative (Fig. 2). The effect leveled off to a constant interference, with respect to sodium sulphate concentration, after 3,500 mg of sodium sulphate was added to the final volume. A minimum of

5 mg of sodium sulphate were required in the final volume to observe the effect.

In the absence of PAM, sodium sulphate had a positive additive effect on the starch-triiodide method results. This effect was observed with as little as 100 mg of sodium sulphate and it leveled off at 8,000 mg of sodium sulphate (Fig. 3). However, the positive additive effect was minimal compared to the negative effect on the PAM reaction. The net result was lower absorbances and high blanks, for standard PAM curves with sodium sulphate present in percent ranges of the final volume.

In order to make the PAM reaction independent of sodium sulphate concentration, 10 ml of 2.3 M (3,370 mg) sodium sulphate were used. This amount produced a high but consistant blank absorbance value. Under these conditions it was possible to study the effect of other interferences under constant ionic strength, assuming that the effect of sodium sulphate was largely due to ionic strength. Hence, any effect from interferences observed in the presence of excess sodium sulphate, could not be attributed to ionic strength. Constant ionic strength conditions adversely affected the sensitivity of PAM standard curves compared to standard conditions, but the method was still linear up to 260 ug of PAM (Fig. 4).

Effect of Divalent Metallic Ions

Calcium was introduced to the method as nitrate and magnesium and zinc as sulphates. Nitrate and sulphate did not interfere in the ranges of metal examined. The result was a small negative effect on colour intensity under conditions of constant PAM concentration (Fig's 5,6 and 7). The effects of the divalent cations were seen with as low as 0.1 mg of metal cation present. With the addition of 10 more mg of metal cation, the colour intensity only dropped 10 % of the actual absorbance due to PAM. The effect was relatively consistant, in terms of absorbance, after about 5 mg. In the presence of excess sodium sulphate the decrease was not seen. This inferred that the small effect observed was due to ionic strength.

Divalent iron, as the sulphate, showed a significant positive effect on colour intensity that was detectable above 0.5 mg of ferrous ion. The effect was independent of ferrous concentration with over 5 mg of ferrous ion present. This was observed both with constant PAM concentration and with no PAM at all (Fig. 8 and Fig. 9 respectively). Further experimentation revealed that the cause of the additive effect was not simply due to oxidation of iodide as the results initially implied.

Two observations, in the study of ferrous ion, led to the hypothesis that more than one effect caused the net additive interference on the method. Firstly, the positive influence

of iron on the colour was intensified under constant ionic strength conditions (Fig. 10). This change in the effect showed that there was a negative ionic strength effect due to iron, however, it was masked by a dominant positive effect. Secondly, an orange-brown colour was observed after bromination of PAM which persisted after the destruction of excess bromine. This colour was characteristic of ferric bromide ($FeBr_3$) (4) inferring that bromine oxidised ferrous to ferric ion probably in a manner similar to the following reaction (5):

$$Br_2 + 2FeSO_4 + H_2SO_4 \text{ -------> } Fe_2(SO_4)_3 + 2HBr$$

Introduction of excess potassium thiocyanate to the method after the destruction of excess bromine, created a dark red colour. This was indicative of the presence of ferric ion and confirmed that ferrous ion was oxidised. The ferric ion produced then reacted with excess bromine to form the orange-brown colour. The same colour was observed when ferric ion was reacted with bromine directly. Thus, small negative effects due to ionic strength and bromine depletion along with a large positive effect due to the development of an orange-brown, colour were all contributing factors to the net positive interference that was observed.

Effect of Trivalent Metallic Ions

In the presence of constant PAM mass, both Al^{3+} as the sulphate and Fe^{3+} as the chloride, showed a slight negative

effect on the reaction of PAM with the reagents. The colour intensity dropped 10 % of the actual absorbance value due to PAM within the addition of the first 2 mg of trivalent metal. After this point, the intensity of the colour developed was independent of trivalent metal concentration (Fig. 11).

These observations contradicted Scoggins' results (1) who found that Al^{3+} enhances the reaction by a factor of two with as little as 0.04 mg of Al^{3+}. Scoggins attributed the effect to decreased steric hinderence on the polymer during the bromination step due to an interaction of Al^{3+} with carboxylate groups on the polymer. Our results showed no such effect in the range from 0 to 10 mg Al^{3+} even when the experiments were repeated with the exact same Al^{3+} to PAM mass ratio used in Scoggins' experiments (Fig. 12). In the presence of excess sodium sulphate, Al^{3+} exhibited no effect on the method results (Fig. 13). Hence, the effect of Al^{3+} was due to ionic strength.

Under constant ionic strength conditions, trivalent iron in the range from 0.1 to 1 mg displayed a significant increase in the absorbance that was proportional to the mass of ferric ion (Fig. 14). The effect became independent of ferric ion over 2 mg of Fe^{3+} (Fig. 15). As was the case with ferrous ion, this phenomenon can be explained by the positive colour interference of ferric bromide (Fig. 16) competing with the negative effects of ionic strength and bromine depletion. However, contrary to ferrous ion, the dominant effects of

ferric ion were negative (Fig. 11).

Effect of Other Cations

Sodium was examined as the sulphate for its effect on the PAM reaction. The only conclusion that was drawn for sodium was that it did not interfere when it was less than 2 mg. This was deduced from the limit of the interference for sodium sulphate in the presence of PAM (Fig. 2). At higher levels of sodium sulphate, where there was an interference, the contribution from sodium and the contribution from sulphate could not be distinguished. Nevertheless, sodium sulphate showed a negative effect on colour intensity due to ionic strength.

Interference from ammonium, as the chloride salt, was examined in a range where effects from chloride were negligible. This was again deduced from the sodium chloride interference curve (Fig. 17). It was found that ammonium had a slight negative effect on the colour intensity in the presence of PAM (Fig. 18). The effect was less obvious, but still observed, when sodium sulphate was present. Hence, the effect was not likely due to ionic strength. Interference could be seen as low as 1 mg ammonium and it did not level off in the range from 0 to 10 mg ammonium. Scoggins (1) found that ammonium in high concentrations interfered by depleting bromine.

Effect of Anions

Chloride and phosphate were studied as their sodium salts and iodide as the potassium salt. The conclusion drawn for chloride was that it does not interfere below 10 mg Cl^- (Fig. 17). The negative effect seen in the presence of PAM with amounts of chloride greater than 10 mg, was attributed to the interference of sodium chloride salt as a whole. When the ionic strength was held constant with excess sodium sulphate, the effect of sodium chloride became a positive interference on the PAM reactions. This implied that part of the effect of sodium chloride was due to changes in ionic strength.

Phosphate was examined in a range where sodium had negligible interference on the PAM reactions with the reagents. The effect of phosphate was slightly negative on the colour intensity. However, it only dropped 3 % of the actual colour intensity due to PAM, with the addition of 10 mg of phosphate (Fig. 19). The same effect was observed under conditions of constant ionic strength. The interference was induced with as low as 1 mg PO_4^{3-} in the final volume.

Nitrate was also studied in a range where sodium had negligible influence on the method. In the absence of PAM, nitrate contributed to colour development when present greater than 5 mg. However, in the presence of PAM, the effect was masked by absorbance developed by PAM even with 10 mg of NO_3^- (Fig. 20). Hence, nitrate produced high absorbance results only for very low concentrations of

polyacrylamide.

Iodide was found to have a direct positive interference on the method in absence of PAM (Fig. 21). There was no change in the effect whether or not the ionic strength was held constant (Fig. 22). The interference could be observed with as low as 0.07 ug of I^- present. Scoggins (1) observed the same effect at pH 3.5, however, he found no colour due to I^- in the pH range from 5.2 to 5.7. Scoggins (1) attributed the effect to direct oxidation of I^- to I_2 by bromine during the bromination step of the method. However, Scoggins' postulation was incomplete since the excess iodine, formed from bromine oxidation of I^-, could not be detected by the leuco crystal violet method (6) with ug quantities of I^- contaminant. In conjunction with direct oxidation of iodide, bromine also reacted to form iodine dibromide by the mechanism (6):

$$2I^- + Br_2 \longrightarrow 2Br^- + I_2$$

$$I_2 + Br_2 \longrightarrow 2IBr$$

$$IBr + Br^- \longrightarrow IBr_2^-$$

IBr_2^- may have been capable of complexing with starch in the same manner as triiodide, which therefore supplemented colour development.

Effect of Organic Contaminants

All of the water soluble organics examined had some sort of effect on the starch-triiodide method results. Oil saturated

water also affected colour intensity, but, not to the same extent as phenol, acetone, humic acid or maleic acid, which were also studied. The nature of the interferences varied greatly.

Phenol interfered with the method results by reacting with bromine to form 2,4,6-tribromophenol, in the following manner (7):

$$(C_6H_5)OH + 3Br_2 \text{ -------> } (C_6H_2)Br_3OH + 3HBr$$

Confirmation of this reaction was observed by depletion of the yellow colour due to bromine which took place after the bromination step and was proportional to phenol concentration. 2,4,6-tribromophenol was soluble in water in amounts up to 70 ppm (8) or up to 3.5 mg in the final volume used in the method. When phenol was present in amounts less that 2 mg, a significant positive interference was observed on colour intensity both in the presence and in the absence of PAM (Fig. 23). This implied that 2,4,6-tribromophenol was oxidising some of the iodide to iodine to produce an additive interference on the colour intensity. The same effects were observed with constant ionic strength both with and without PAM. The positive interference was not detected when phenol was less than 0.01 mg in the final solution.

When between 2 and 5 mg of phenol were present, the first signs of a white precipitate were observed after the

bromination step. At this point, the intensity of the developed colour dropped rapidly with increasing phenol concentration (Fig. 24). This may have been caused by a combination of the colour becoming trapped in the filtered precipitate and the loss of bromine due to the bromination of phenol. At amounts of phenol greater than 20 mg, a second smaller peak in colour intensity was consistantly observed. These phenomena occurred both in the presence and in the absence of PAM as well as with and without constant ionic strength.

Acetone had a linear, negative effect on colour intensity in the presence of PAM (Fig. 25). The interference was observed with as low as 4 mg of acetone. Acetone totally eliminated the colour due to the PAM reaction when present greater than 200 mg. The effect was intensified under conditions of constant ionic strength.

Maleic acid present in amounts over 10 mg had an effect on the rate of the reaction and also consumed bromine. The consumption of bromine was observed by the loss of yellow colour during bromination that was proportional to maleic acid concentration. When more than 10 mg of maleic acid were present, the development of the colour due to polyacrylamide was initially much slower. Twenty minutes after the addition of the cadmium iodide-starch reagent, the development of the colour accelerated until all the I^- was oxidised. (Fig.

26). Absorbance readings taken between 15 and 20 minutes after the addition of the last reagent, produced reliable results independent of maleic acid concentration (Fig. 27). A similar effect was observed under constant ionic strength conditions, however, colour developed rapidly and reliable absorbance readings could not be obtained after any extended, elapsed time.

The presence of less than 10 mg of maleic acid produced a slight negative interference on the colour intensity. With the addition of 0.5 mg of maleic acid, colour intensity dropped 10 % of the actual intensity due to PAM. However, with additions greater than 0.5 mg of maleic acid, the colour intensity was independent of maleic acid concentration (Fig. 28). No interference was observed with less than 0.01 mg of maleic acid. Under conditions of constant ionic strength, the effect was opposite but less dramatic which implied that the effect was due to ionic strength (Fig. 28).

Humic acid had a significant positive effect on the colour intensity with and without PAM (Fig. 29). This led to the conclusion that humic acid oxidised iodide to iodine. The effect could be observed with a minimum of 0.005 mg of humic acid and was found to be independent of ionic strength conditions. The colour of humic acid in solution also interfered at levels as low as 0.04 mg of humic acid. Therefore, absorbance measurements were taken against sample blanks.

The effect on the colour intensity of saturated oil solutions in water was slightly negative. The oil solutions were prepared by vigorously stirring a 1:10 oil to water mixture overnight then decanting the oil layer. The oil used was Edward supergrade "A" vacuum pump oil. The solution was left to sit 2 hours after stirring and aliquots were taken from the water layer. The effect of adding 10 ml of saturated oil solution was a drop of 10 % of the original colour intensity developed by the PAM (Fig. 30). A sample blank was subtracted from the absorbance readings to account for turbidity. Absorbance results under constant ionic strength were more erratic but they exhibited the same trend.

Effect of Oxidising Contaminants

The effect of typical oxidants for iodide were not studied. However, Scoggins (1) found that hydrogen peroxide and nitrite where both oxidised by bromine added during the method. It followed that their only effect on the method would have been due to the depletion of bromine.

TABLE 2
EFFECT OF INTERFERENCES ON THE STARCH-TRIIODIDE METHOD

CONTAMINANT	MIN. AMT. FOR AN EFFECT	EFFECT ON COLOUR INTENSITY	NATURE OF INTERFERENCE	FIGURE #
Sodium Sulphate	5 mg	negative	ionic strength	2,3,4
Divalent Calcium	0.1 mg	negative	ionic strength	5
Divalent Magnesium	0.1 mg	negative	ionic strength	6
Divalent Zinc	0.1 mg	negative	ionic strength	7
Ferrous Ion	0.5 mg	net positive	ferric bromide abs. ionic strength bromine depletion	8,9,10
Ferric Ion	0.01 mg	net positive	ferric bromide abs. ionic strength bromine depletion	11,12, 14,15
Trivalent Aluminium	0.1 mg	negative	ionic strength	11,12,13
Sodium	2 mg	negative	ionic strength	18
Ammonium	1 mg	negative	bromine depletion	19
Chloride	10 mg	negative	ionic strength	18
Phosphate	1 mg	negative	unknown	20
Nitrate	5 mg	positive	colour development	20a
Iodide	7exp(-5)mg	positive	colour development	21,22
Phenol	0.01 mg	positive	colour development	23,24
Acetone	4 mg	negative	unknown	25
Maleic Acid	0.01 mg	negative	ionic strength	27,28
Maleic Acid	>10 mg	positive	colour development	25a,26
Humic Acid	0.04 mg	positive	colour development	29
Oil	--	negative	unknown	30

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PART II

EFFECT OF pH ON COLOUR INTENSITY
Figure 1

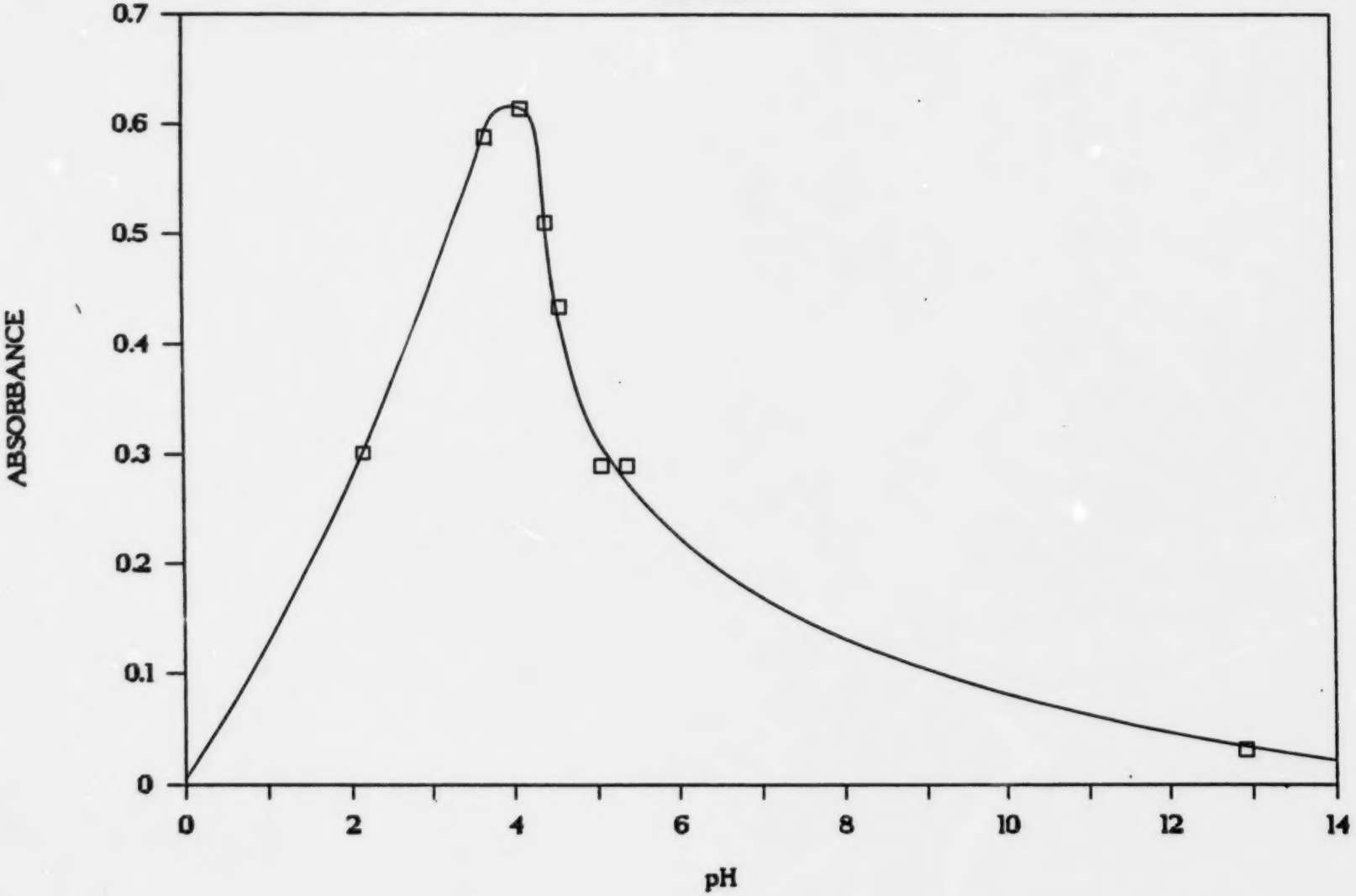
Final Adjusted pH	Absorbance
2.15	0.301
3.67	0.589
4.12	0.614
4.41	0.511
4.56	0.434
5.06	0.290
5.37	0.290
12.90	0.032

Experimental Conditions:

Experiment #..... STI 27
Final Volume..... 46 ml
Mass PAM..... 148 ug
Path Length..... 1 cm
Wavelength..... 610 nm

EFFECT OF pH ON COLOUR INTENSITY

FIGURE 1



PART II

EFFECT OF SODIUM SULPHATE
Figure 2

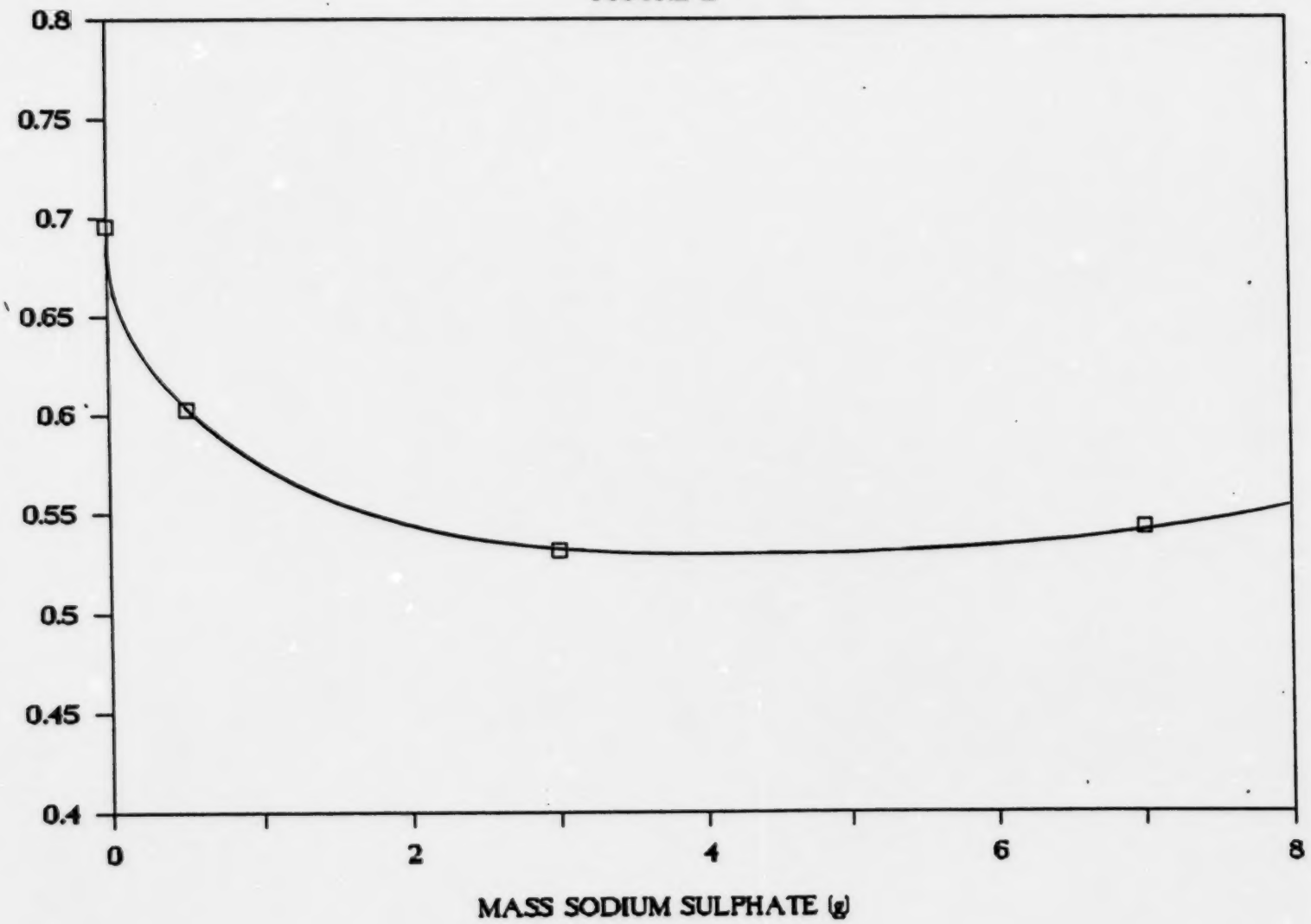
Mass of Sodium Sulphate (g)	Absorbance
0.0	0.696
0.5	0.603
3.0	0.532
7.0	0.543

Experimental Conditions:

Experiment #.....	STI 5
Final Volume.....	46 ml
Dry Mass PAM.....	148 ug
Path Length.....	1 cm
Wavelength.....	610 nm

EFFECT OF SODIUM SULPHATE

FIGURE 2



PART II

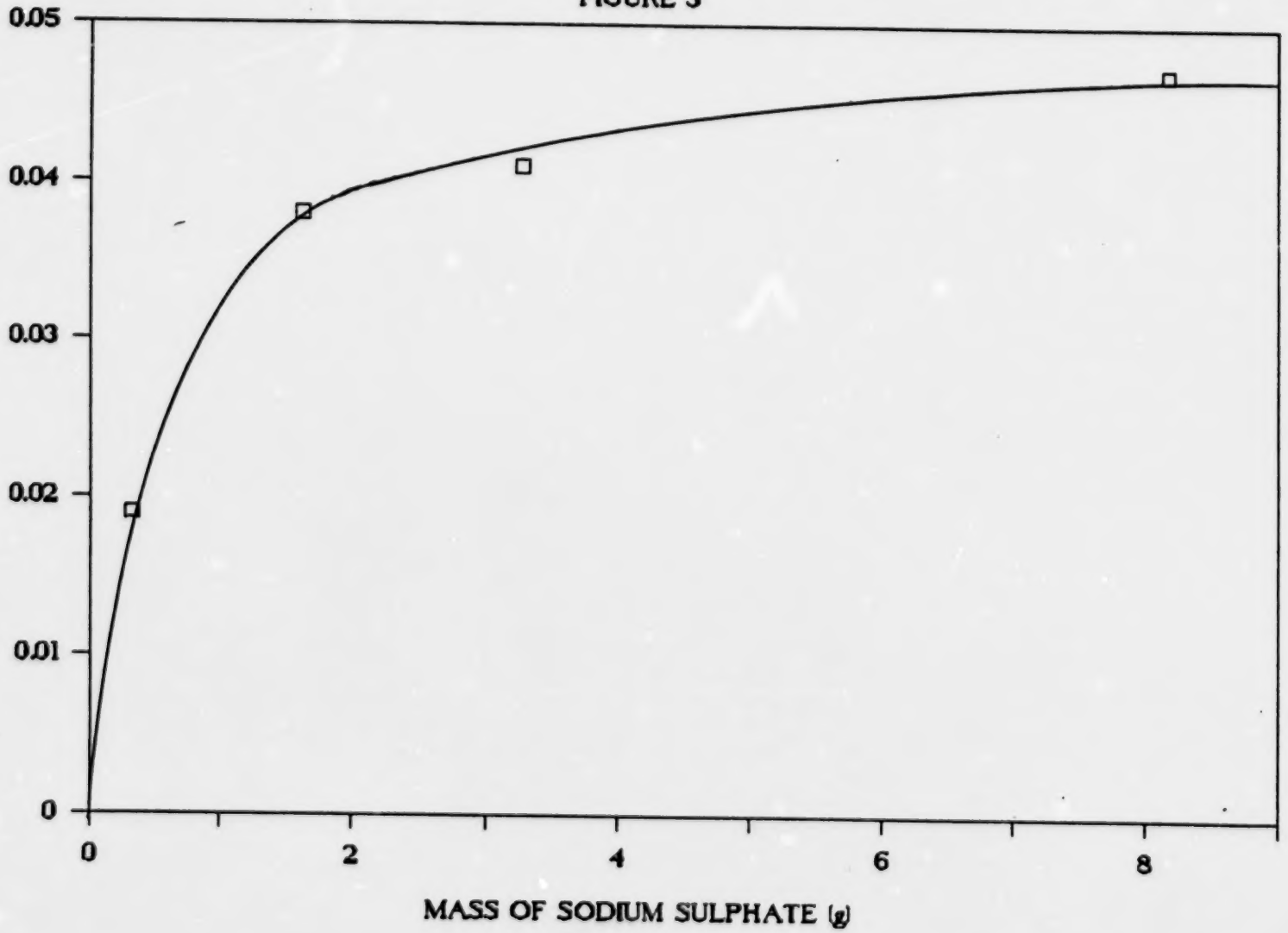
EFFECT OF SODIUM SULPHATE;
WITHOUT PAM
Figure 3

Mass of Sodium Sulphate (g)	Absorbance
0.33	0.019
1.64	0.038
3.27	0.041
8.18	0.047

Experimental Conditions:
Experiment #..... STI 49
Final Volume..... 46 ml
Dry Mass PAM..... 0 ug
Path Length..... 1 cm
Wavelength..... 610 nm

EFFECT OF SODIUM SULPHATE: WITHOUT PAM

FIGURE 3



PART II

PAM CONCENTRATION CURVE;
CONSTANT IONIC STRENGTH
Figure 4

#	Mass of PAM (ug)	Absorbance Minus Intercept
1	0.0	0.010
2	18.4	0.042
3	31.5	0.050
4	59.1	0.142
5	110.9	0.219
6	157.4	0.339
7	236.7	0.489
8	295.8	0.585
9	314.9	0.636

Experimental Conditions:

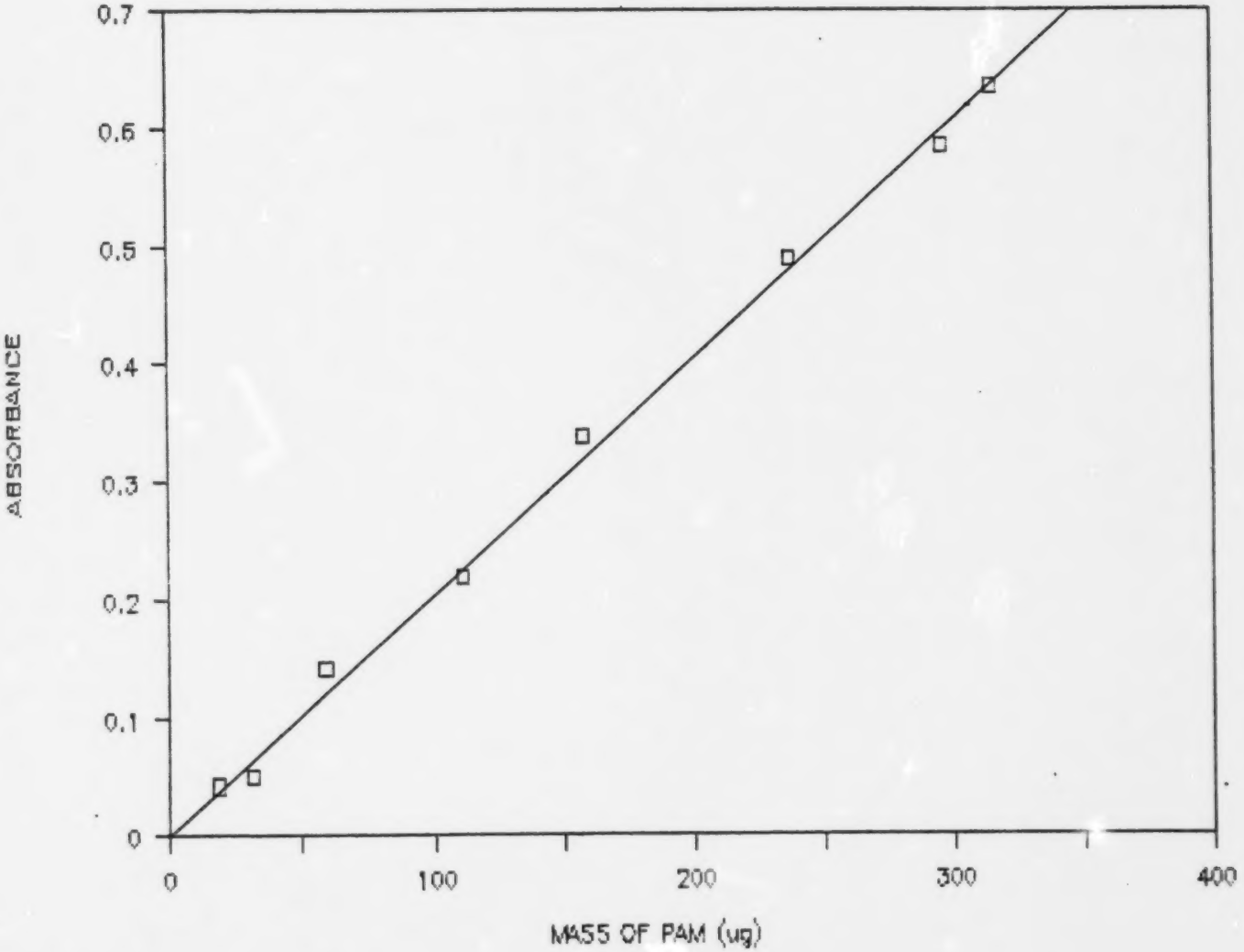
Experiment #.....	STI 6
Final Volume.....	46 ml
Mass of Sodium Sulphate...	3.4 g
Path Length.....	1 cm
Wavelength.....	610 nm

Linear Statistics:

Points Used	2-9
Intercept.....	0.081
Correlation Coefficient.....	0.999
1/Slope.....	570.7

PAM CURVE; CONSTANT IONIC STRENGTH

FIGURE 4



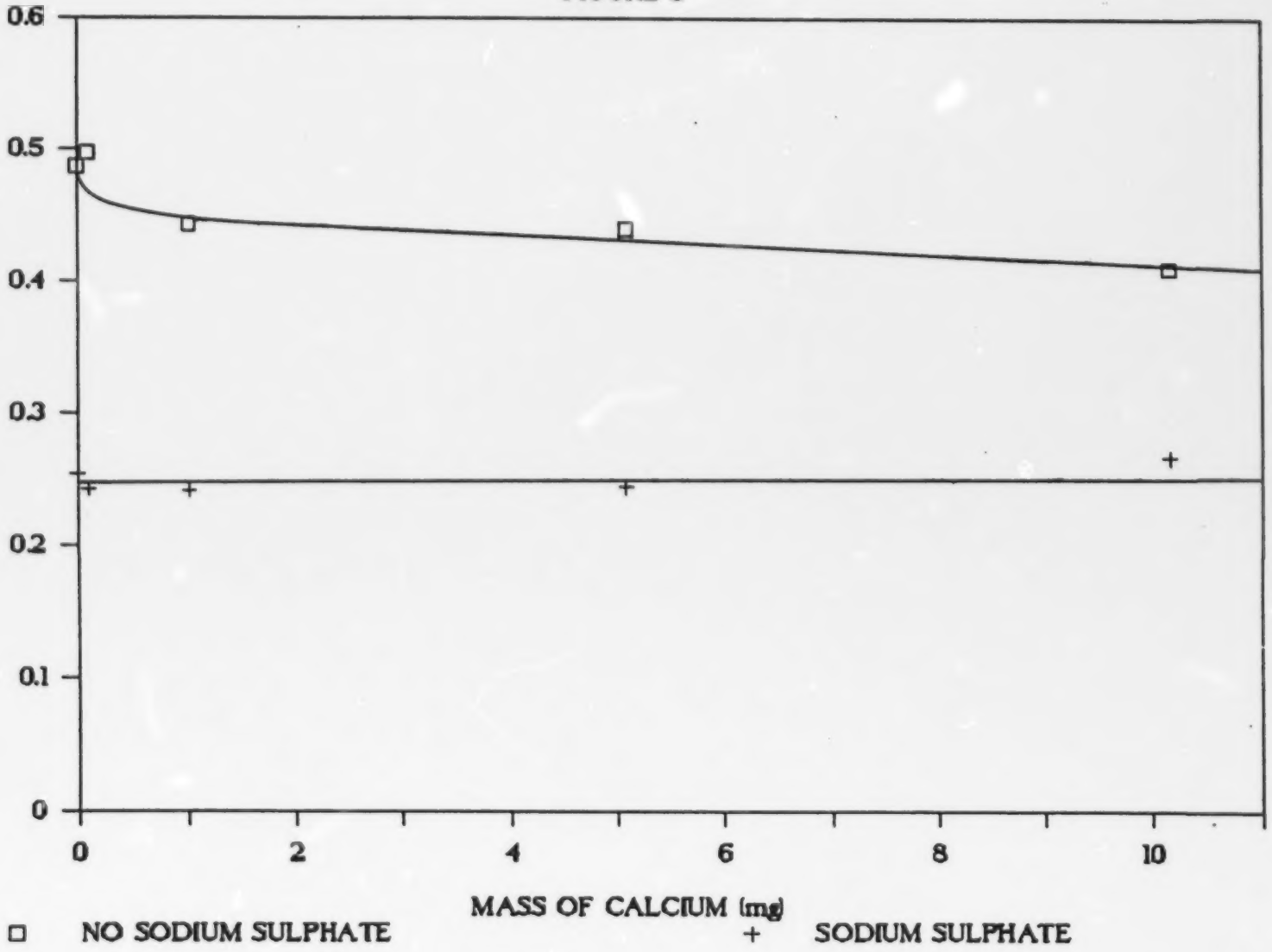
PART II

EFFECT OF CALCIUM
Figure 5

Mass of Divalent Calcium (mg)	Absorbance: Constant Ionic Strength	Absorbance: Standard Conditions
0.000	0.255	0.487
0.102	0.243	0.498
1.016	0.242	0.444
5.080	0.245	0.440
10.160	0.268	0.411
Experimental Conditions:		
Experiment #	STI 16	STI 15
Final Volume	46 ml	46 ml
Dry Mass PAM	148 ug	148 ug
Mass Sodium Sulphate	3.4 g	0 g
Path Length	1 cm	1 cm
Wavelength	610 nm	610 nm

EFFECT OF CALCIUM

FIGURE 5



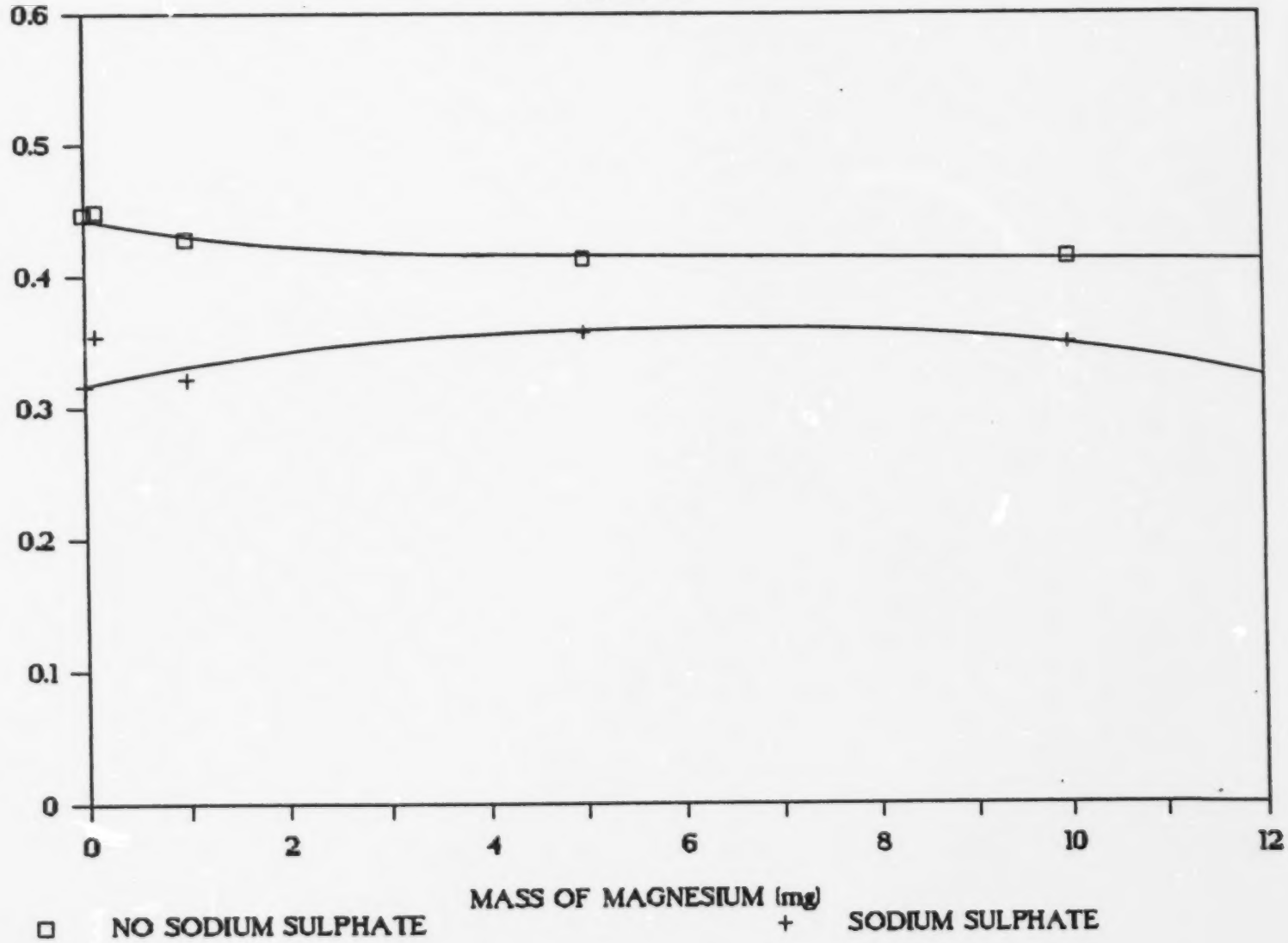
PART II

EFFECT OF MAGNESIUM
Figure 6

Mass of Divalent Magnesium (mg)	Absorbance: Constant Ionic Strength	Absorbance: Standard Conditions
0.0	0.317	0.447
0.1	0.355	0.449
1.0	0.322	0.429
5.0	0.358	0.414
10.0	0.350	0.415
Experimental Conditions:		
Experiment #	STI 18	STI 17
Final Volume	46 ml	46 ml
Dry Mass PAM	148 ug	148 ug
Mass Sodium Sulphate	3.4 g	0 g
Path Length	1 cm	1 cm
Wavelength	610 nm	610 nm

EFFECT OF MAGNESIUM

FIGURE 6



PART II

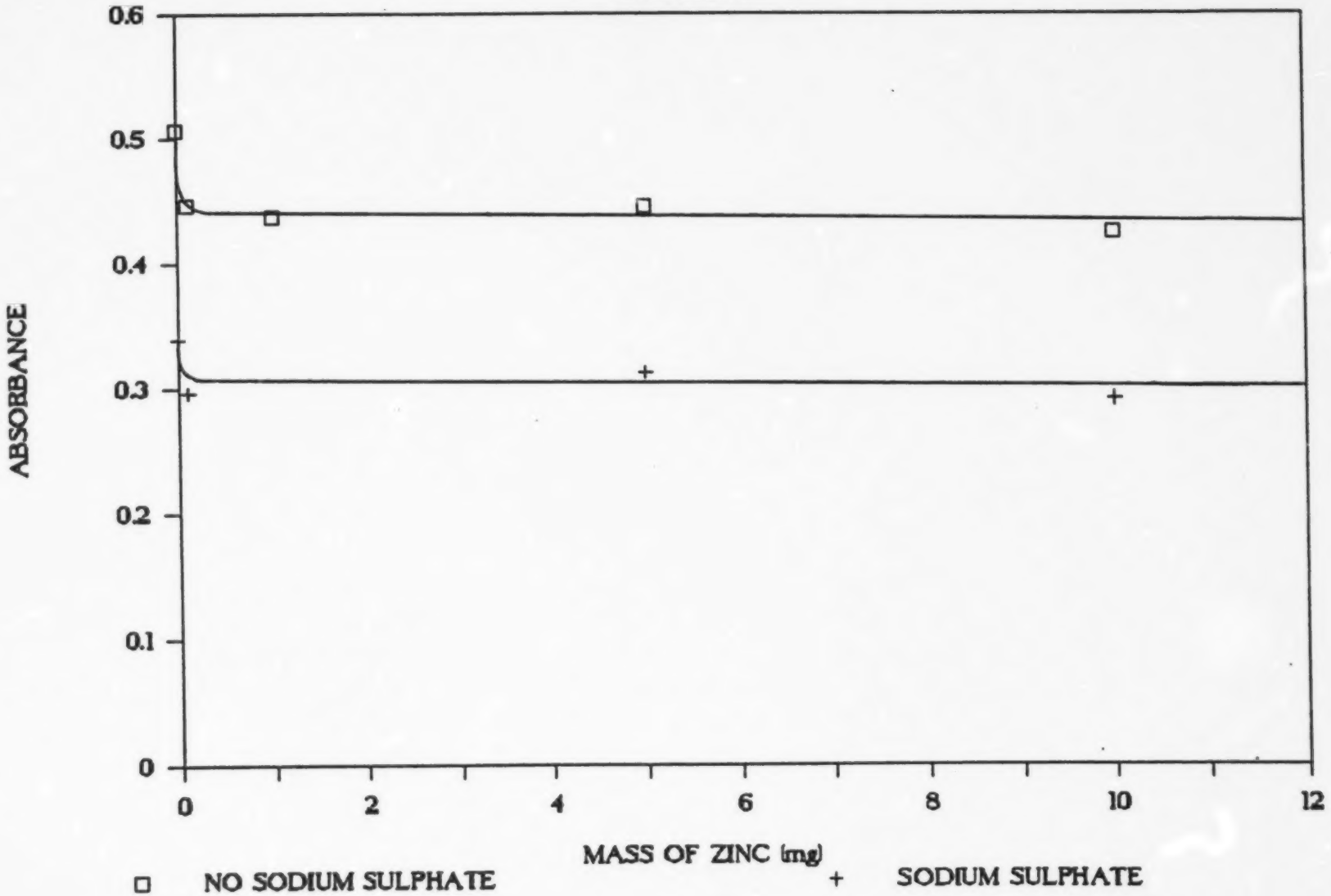
EFFECT OF ZINC
Figure 7

Mass of Divalent Zinc (mg)	Absorbance: Constant Ionic Strength	Absorbance: Standard Conditions
0.0	0.340	0.507
0.1	0.297	0.447
1.0	1000.000	0.438
5.0	0.313	0.446
10.0	0.293	0.425
Experimental Conditions:		
Experiment #	STI 14	STI 13
Final Volume	46 ml	46 ml
Dry Mass PAM	148 ug	148 ug
Mass Sodium Sulphate	3.4 g	0 g
Path Length	1 cm	1 cm
Wavelength	610 nm	610 nm

NOTE: When an absorbance value was not obtained for a given mass of zinc, an arbitrary absorbance value of 1000 was entered in the table.

EFFECT OF ZINC

FIGURE 7



PART II

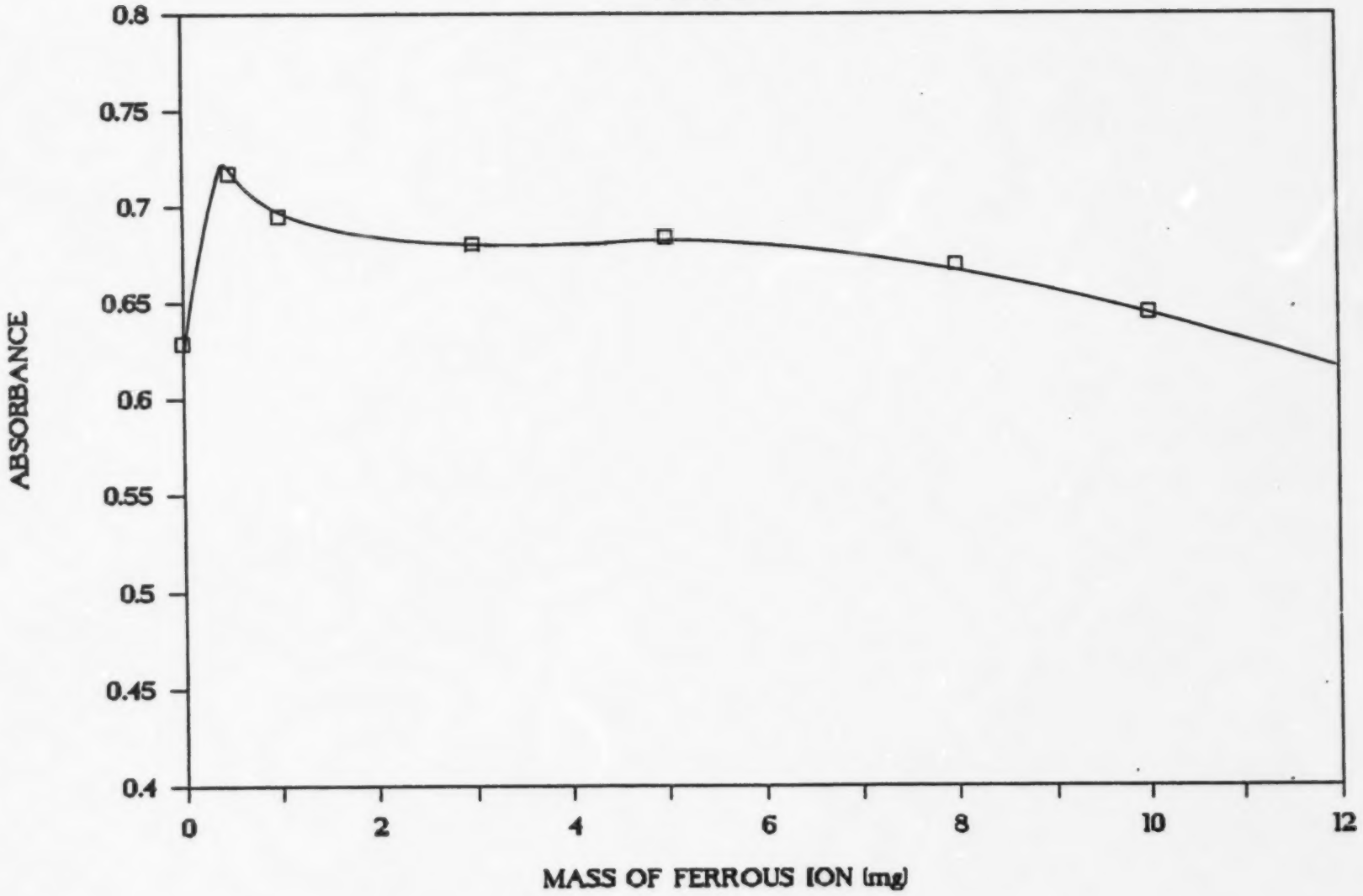
EFFECT OF FERROUS ION
Figure 8

Mass of Ferrous Ion (mg)	Absorbance
0.0	0.629
0.5	0.717
1.0	0.695
3.0	0.681
5.0	0.684
8.0	0.670
10.0	0.645

Experimental Conditions:
- Experiment #..... STI 73
- Final Volume..... 46 ml
- Dry Mass PAM..... 218 ug
- Path Length..... 1 cm
- Wavelength..... 610 nm

EFFECT OF FERROUS ION

FIGURE 8



PART II

EFFECT OF FERROUS ION;
NO PAM
Figure 9

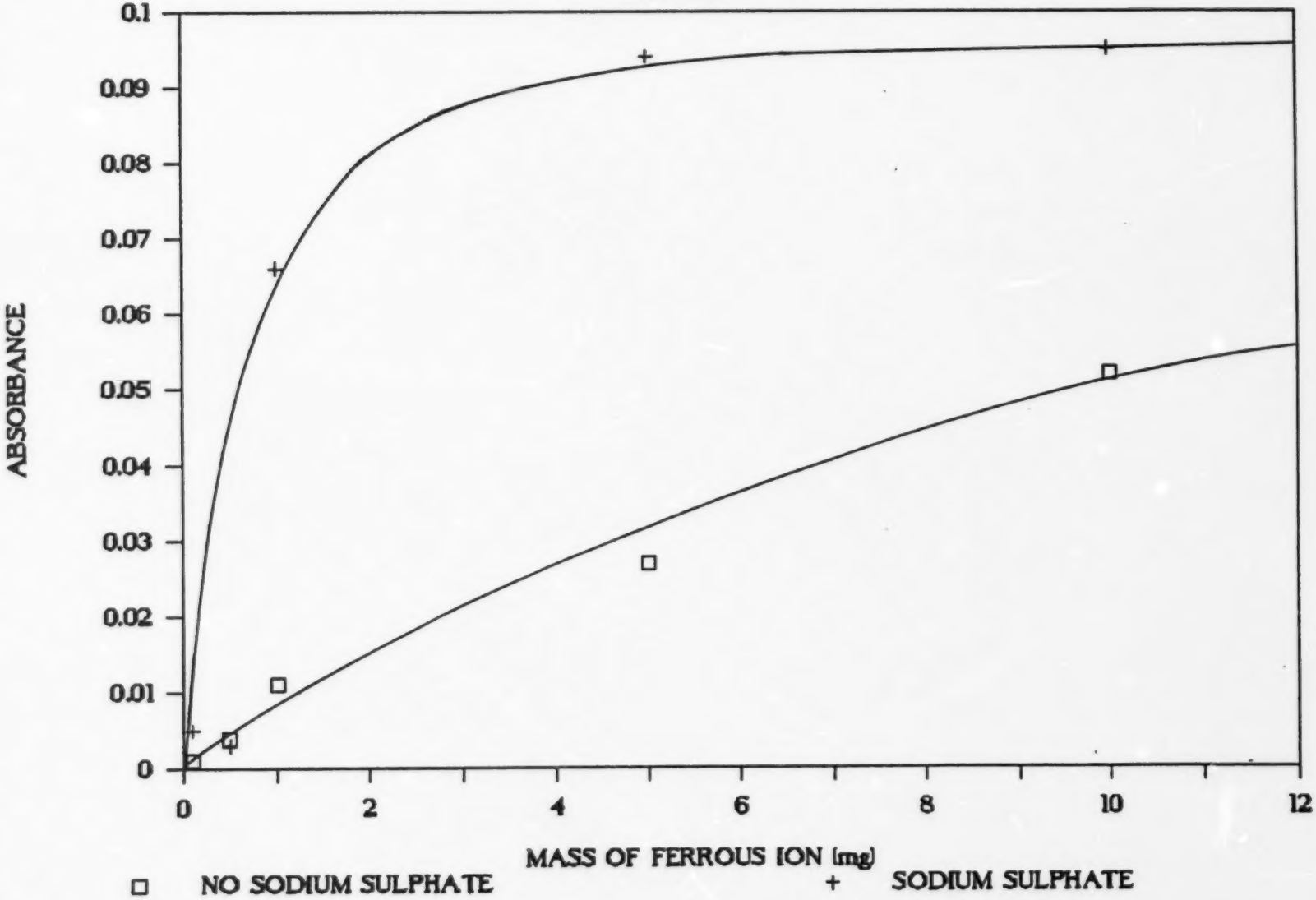
Mass of Ferrous Ion (mg)	Absorbances			
	Constant Ionic Strength		Standard Conditions	
	Abs	Abs-Blk *	Abs	Abs-Blk *
0.1	0.025	0.005	0.017	0.001
0.5	0.023	0.003	0.020	0.004
1.0	0.086	0.066	0.027	0.011
5.0	0.114	0.094	0.043	0.027
10.0	0.123	0.095	0.082	0.052

Experimental Conditions:		
Experiment #	STI 32	STI 31
Final Volume	46 ml	46 ml
Reagent Blank Absorbance	0.020	0.016
Dry Mass PAM	0 ug	0 ug
Mass Sodium Sulphate	3.4 g	0 g
Path Length	1 cm	1 cm
Wavelength	610 nm	610 nm

* Sample blank and reagent blank were subtracted to account for the colour of ferrous ion and reagent absorbance respectively.

EFFECT OF FERROUS ION: NO PAM

FIGURE 9



PART II

EFFECT OF FERROUS ION;
CONSTANT IONIC STRENGTH
Figure 10

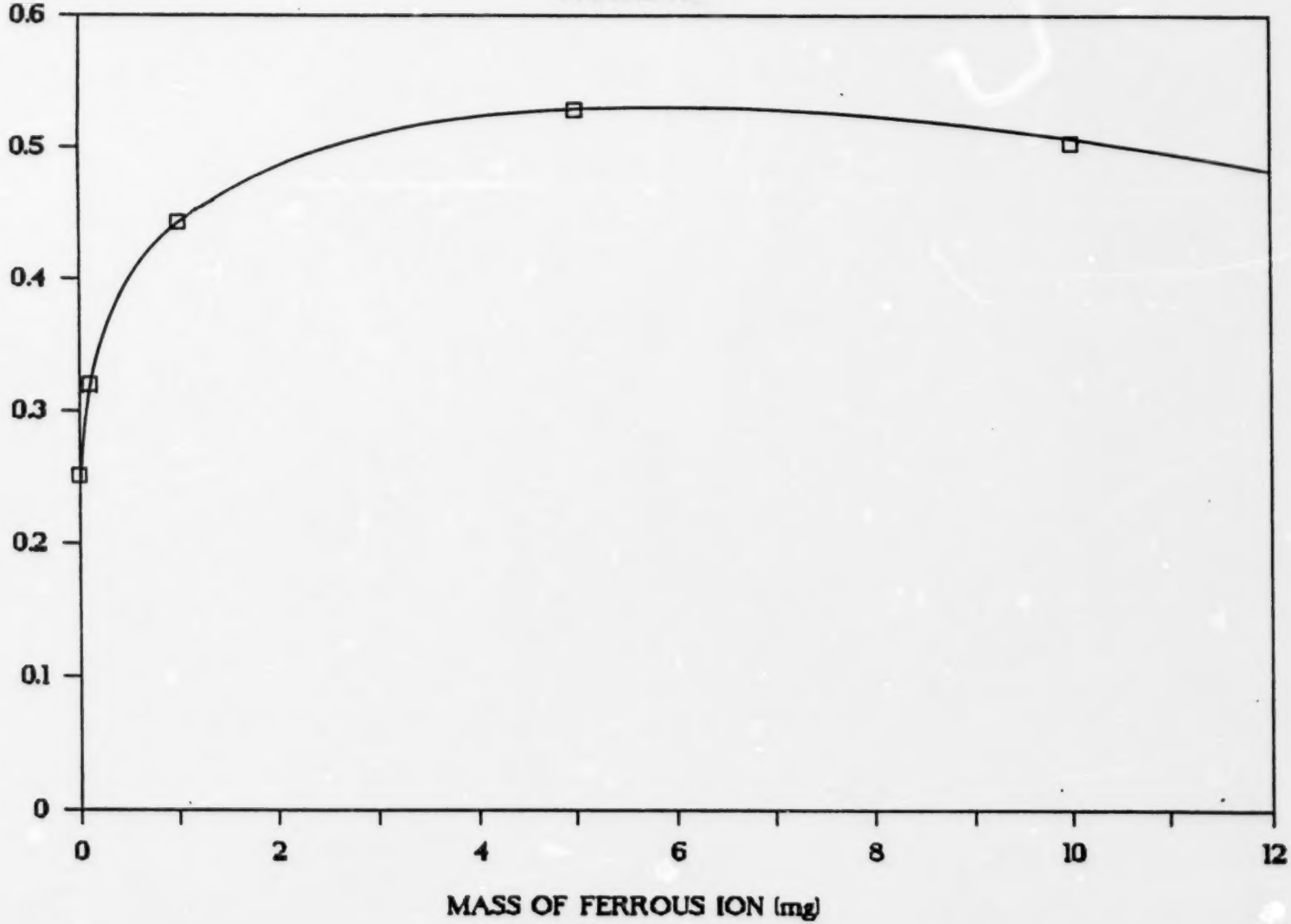
Mass of Ferrous Ion (mg)	Absorbance
0.0	0.251
0.1	0.321
1.0	0.444
5.0	0.529
10.0	0.504

Experimental Conditions:

Experiment #.....	STI 12
Final Volume.....	46 ml
Dry Mass PAM.....	148 ug
Mass Sodium Sulphate.....	3.4 g
Path Length.....	1 cm
Wavelength.....	610 nm

EFFECT OF Fe 2+;CONSTANT IONIC STRENGTH

FIGURE 10



PART II

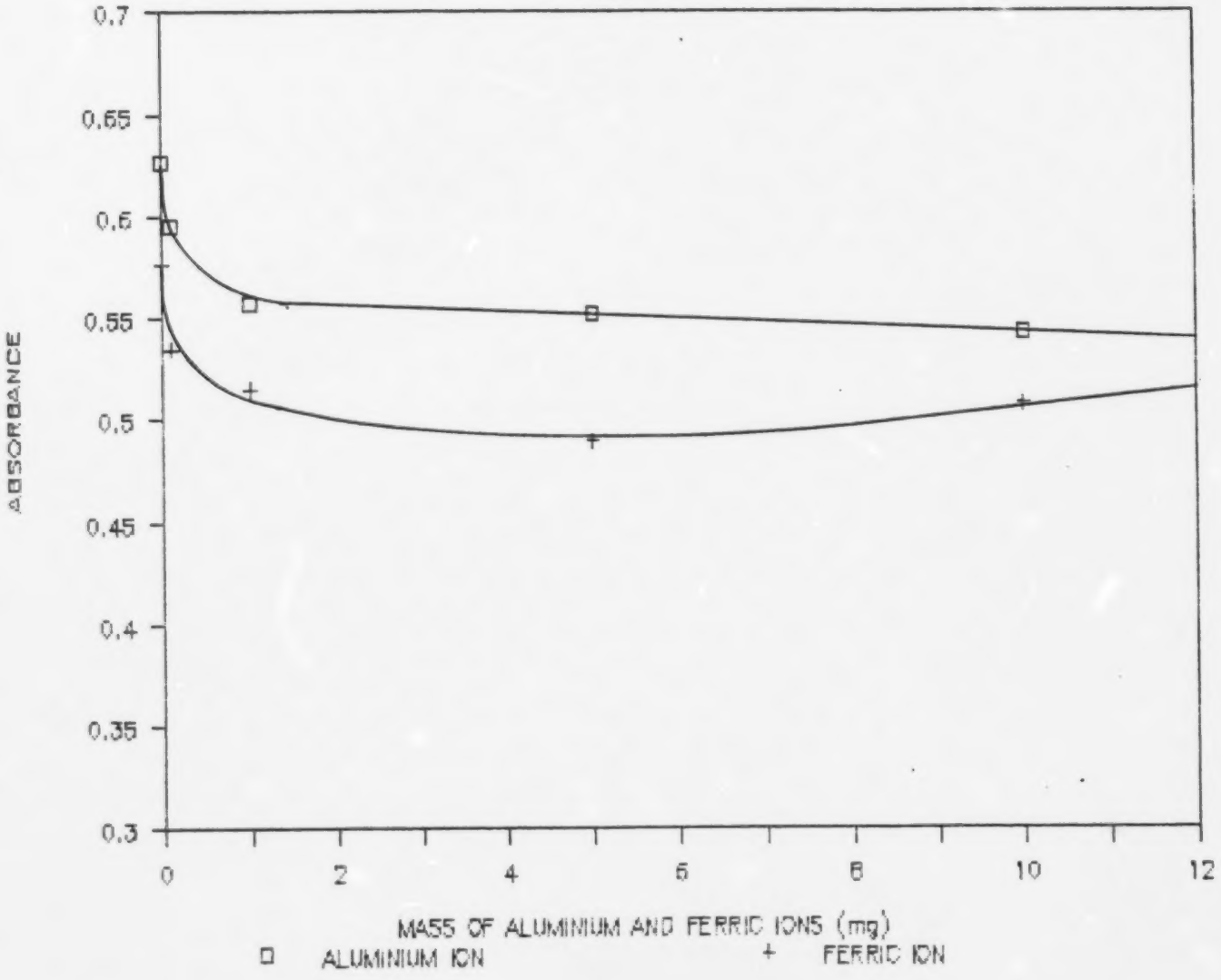
EFFECT OF ALUMINIUM AND FERRIC IONS
Figure 11

Mass of Trivalent Metal (mg)	Absorbance	
	Trivalent Aluminium	Trivalent Iron
0.0	0.627	0.576
0.1	0.595	0.535
1.0	0.557	0.515
5.0	0.552	0.490
10.0	0.543	0.508

Experimental Conditions:		
Experiment #	STI 21	STI 22
Final Volume	46 ml	46 ml
Dry Mass PAM	148 ug	148 ug
Mass Sodium Sulphate	0 g	0 g
Path Length	1 cm	1 cm
Wavelength	610 nm	610 nm

EFFECT OF ALUMINIUM AND FERRIC IONS

FIGURE 11



PART II

EFFECT OF ALUMINIUM AND FERRIC IONS
(Low Mass Range)
Figure 12

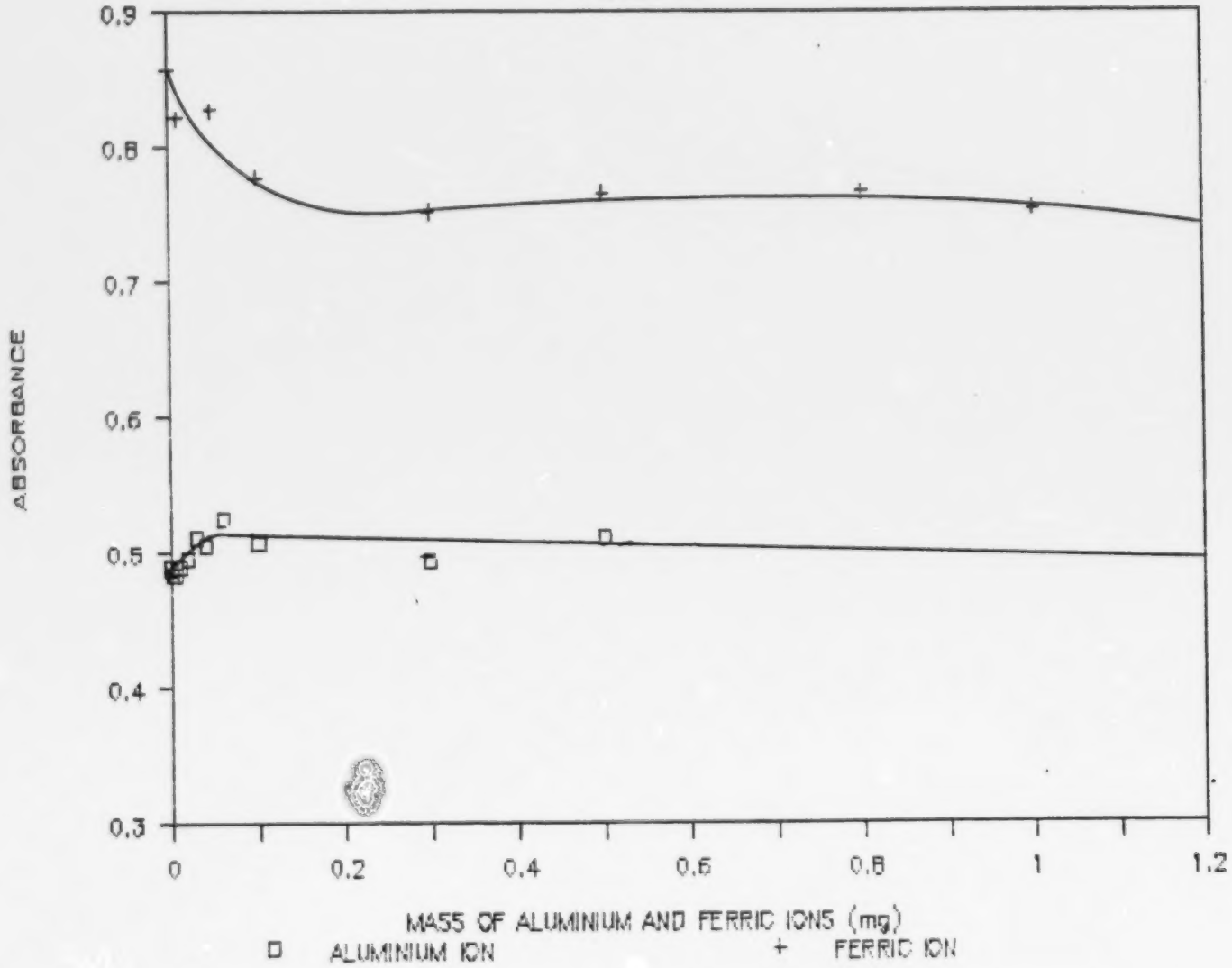
Mass of Trivalent Metal (mg)	Absorbance	
	Trivalent Aluminium	Trivalent Iron
0.000	0.489	0.857
0.001	0.484	0.857
0.005	0.484	1000.000
0.010	0.490	0.822
0.020	0.496	1000.000
0.030	0.511	1000.000
0.040	0.506	1000.000
0.050	1000.000	0.828
0.060	0.525	1000.000
0.100	0.508	0.778
0.300	0.495	0.752
0.500	0.512	0.766
0.800	1000.000	0.767
1.000	1000.000	0.754

Experimental Conditions:		
Experiment #	STI 69	STI 71
Final Volume	46 ml	46 ml
Dry Mass PAM	179 ug	179 ug
Mass Sodium Sulphate	0 g	0 g
Path Length	1 cm	1 cm
Wavelength	610 nm	610 nm

NOTE: When an absorbance value was not obtained for a given mass of metal, an arbitrary absorbance value of 1000 was entered in the table.

EFFECT OF ALUMINIUM AND FERRIC IONS

FIGURE 12



PART II

EFFECT OF ALUMINIUM;
CONSTANT IONIC STRENGTH
Figure 13

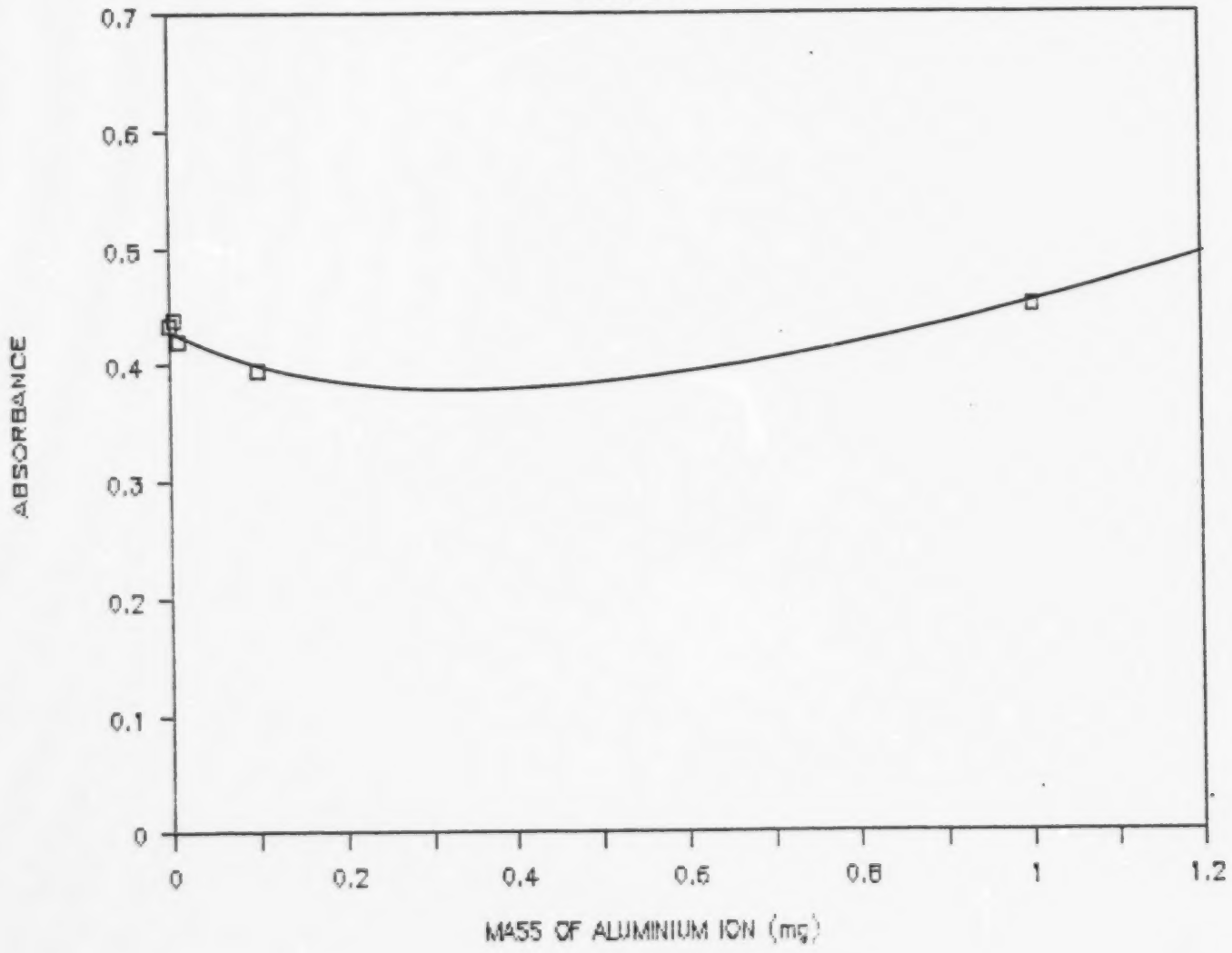
Mass of Aluminium (mg)	Absorbance
0.000	0.435
0.005	0.440
0.010	0.420
0.100	0.395
1.000	0.450

Experimental Conditions:

Experiment #.....	STI 24
Final Volume.....	46 ml
Dry Mass PAM.....	148 ug
Mass Sodium Sulphate.....	3.4 g
Path Length.....	1 cm
Wavelength.....	610 nm

EFFECT OF A13+; CONSTANT IONIC STRENGTH

FIGURE 13



PART II

FERRIC ION;
CONSTANT IONIC STRENGTH
Figure 14

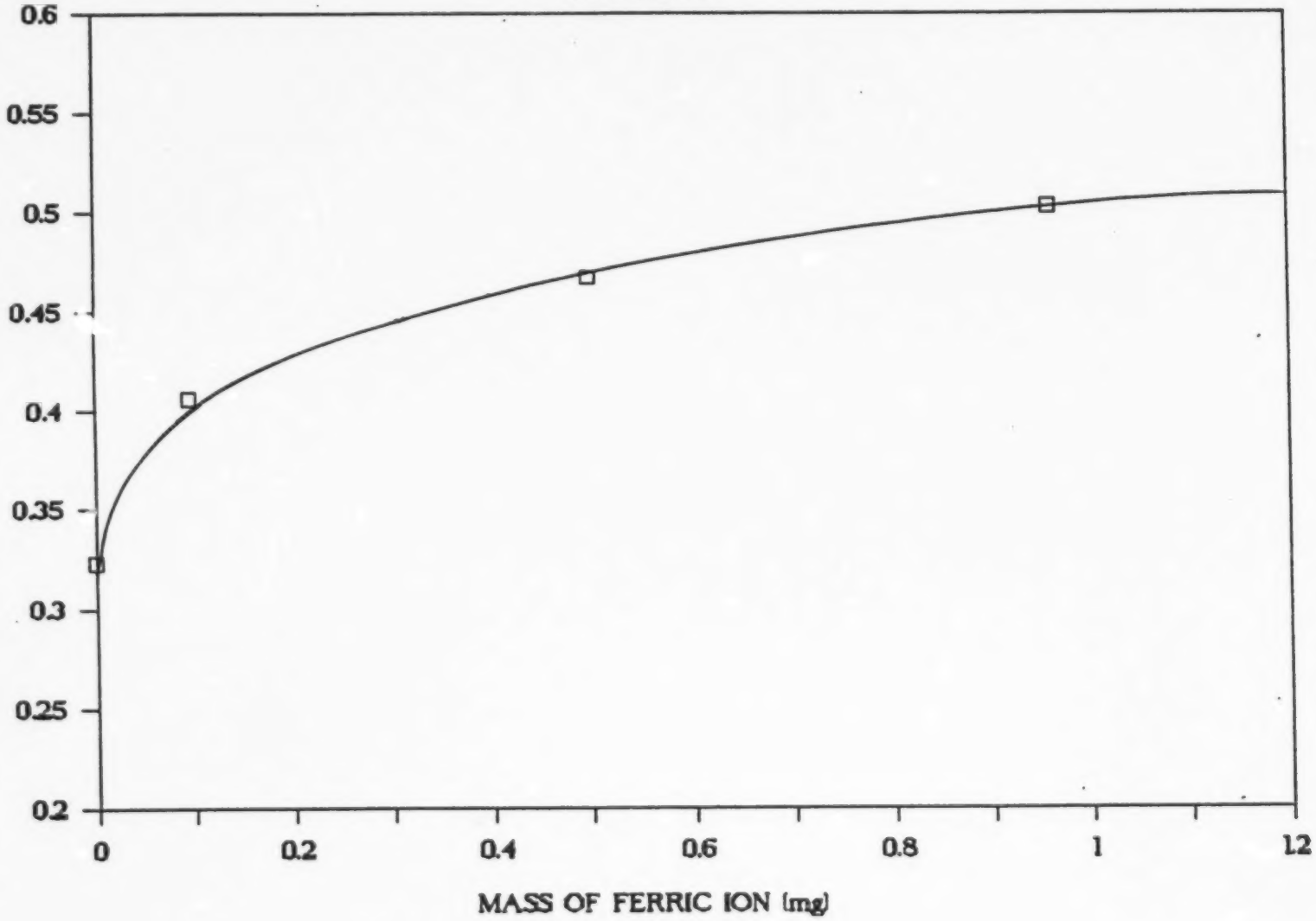
Mass of Ferric Ion (mg)	Absorbance
0.000	0.323
0.096	0.406
0.498	0.467
0.958	0.503

Experimental Conditions:

Experiment #.....	STI 39
Final Volume.....	46 ml
Dry Mass PAM.....	148 ug
Mass Sodium Sulphate.....	3.4 g
Path Length.....	1 cm
Wavelength.....	610 nm

FERRIC ION: CONSTANT IONIC STRENGTH

FIGURE 14



PART II

FERRIC ION;
CONSTANT IONIC STRENGTH
Figure 15

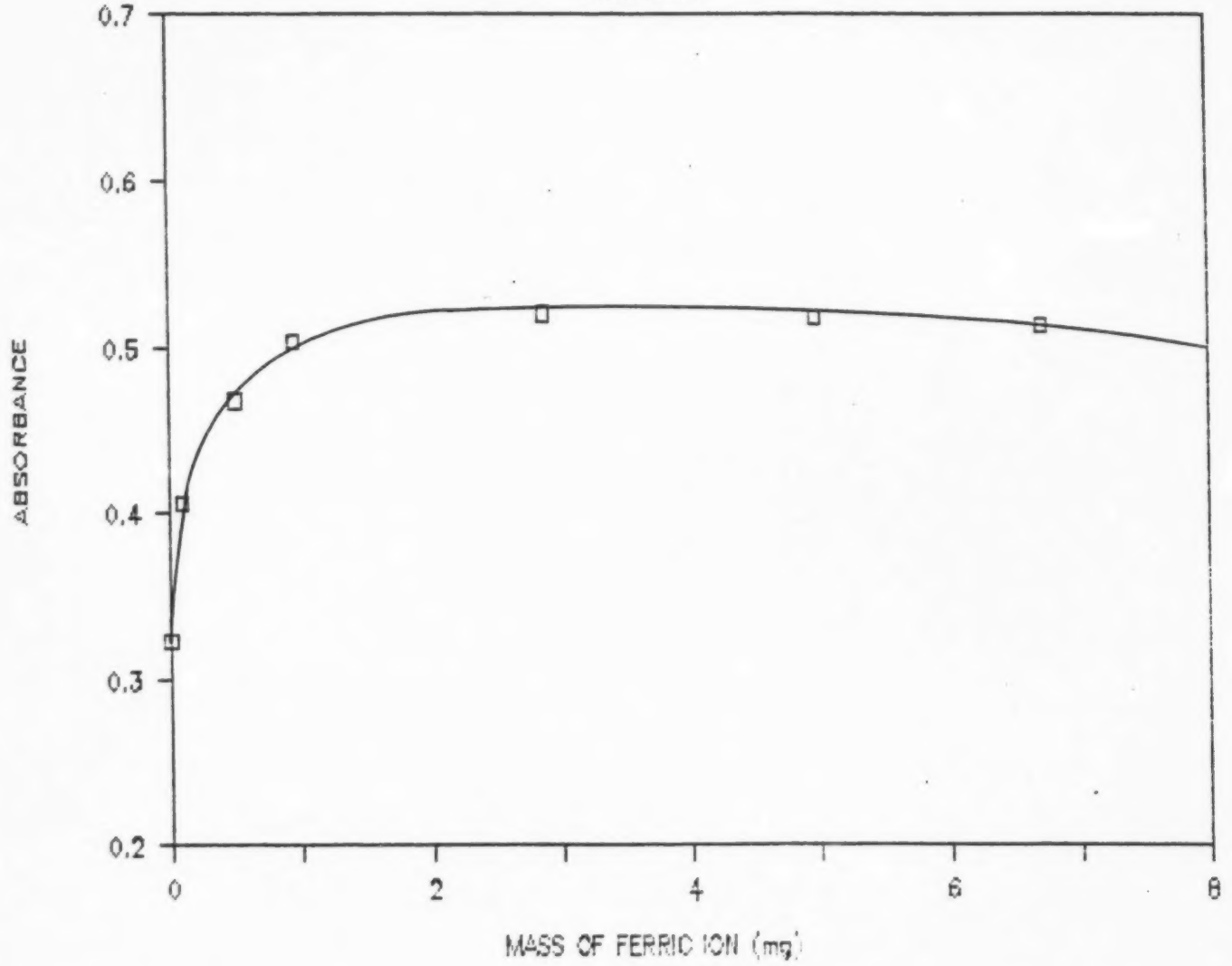
Mass of Ferric Ion (mg)	Absorbance
0.000	0.323
0.096	0.406
0.498	0.467
0.958	0.503
2.874	0.520
4.979	0.517
6.706	0.513

Experimental Conditions:

Experiment #.....	STI 39
Final Volume.....	46 ml
Dry Mass PAM.....	148 ug
Mass Sodium Sulphate.....	3.4 g
Path Length.....	1 cm
Wavelength.....	610 nm

FERRIC ION; CONSTANT IONIC STRENGTH

FIGURE 15



PART II

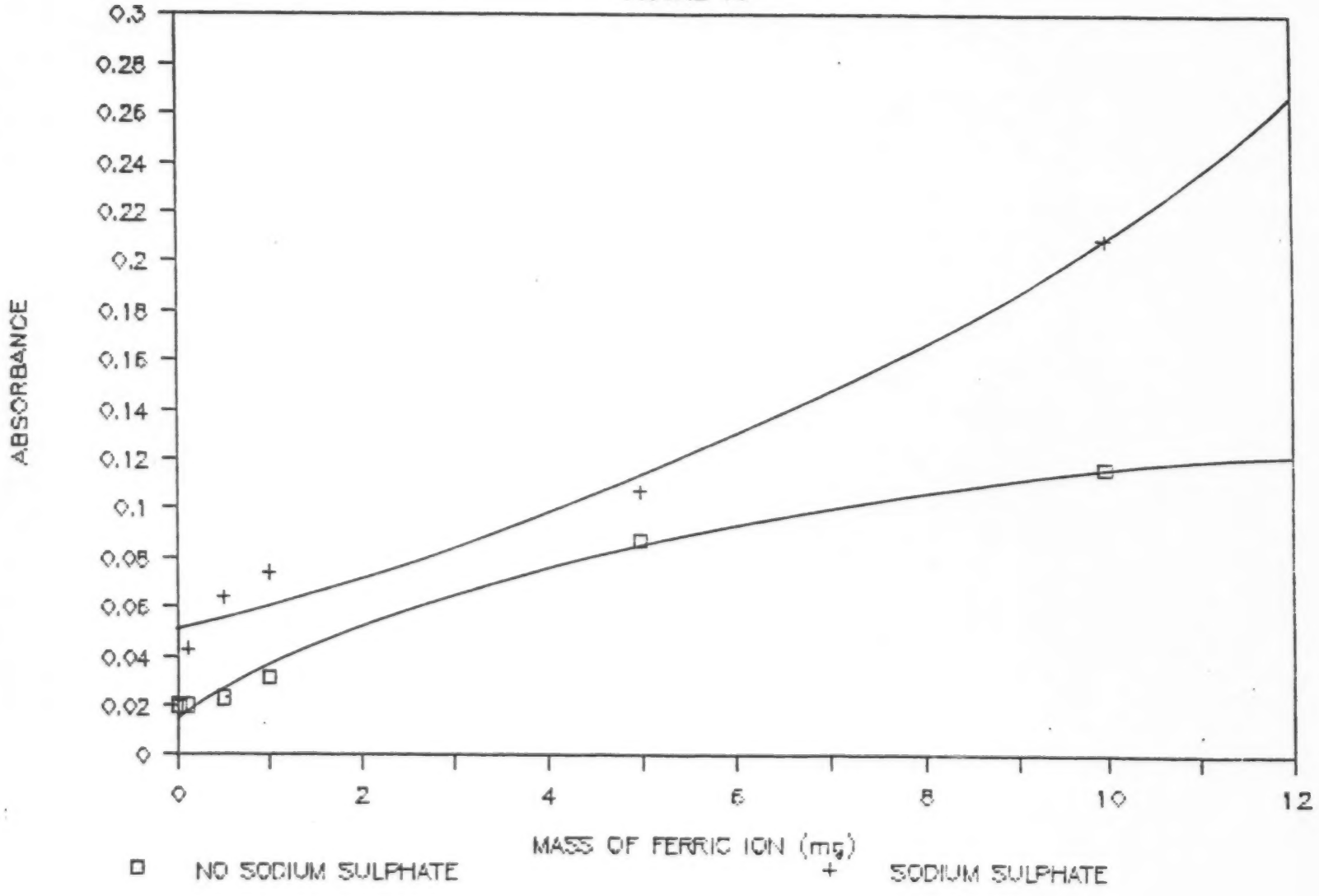
EFFECT OF Fe3+;
WITHOUT PAM
Figure 16

Mass of Trivalent Iron (mg)	Absorbance: Constant Ionic Strength	Absorbance: Standard Conditions
0.000	0.022	0.020
0.100	0.043	0.020
0.498	0.064	0.023
0.996	0.074	0.031
4.979	0.107	0.087
9.958	0.209	0.117

Experimental Conditions:		
Experiment #	STI 30	STI 29
Final Volume	46 ml	46 ml
Dry Mass PAM	0 ug	0 ug
Mass Sodium Sulphate	3.4 g	0 g
Path Length	1 cm	1 cm
Wavelength	610 nm	610 nm

EFFECT OF Fe3+; WITHOUT PAM

FIGURE 16



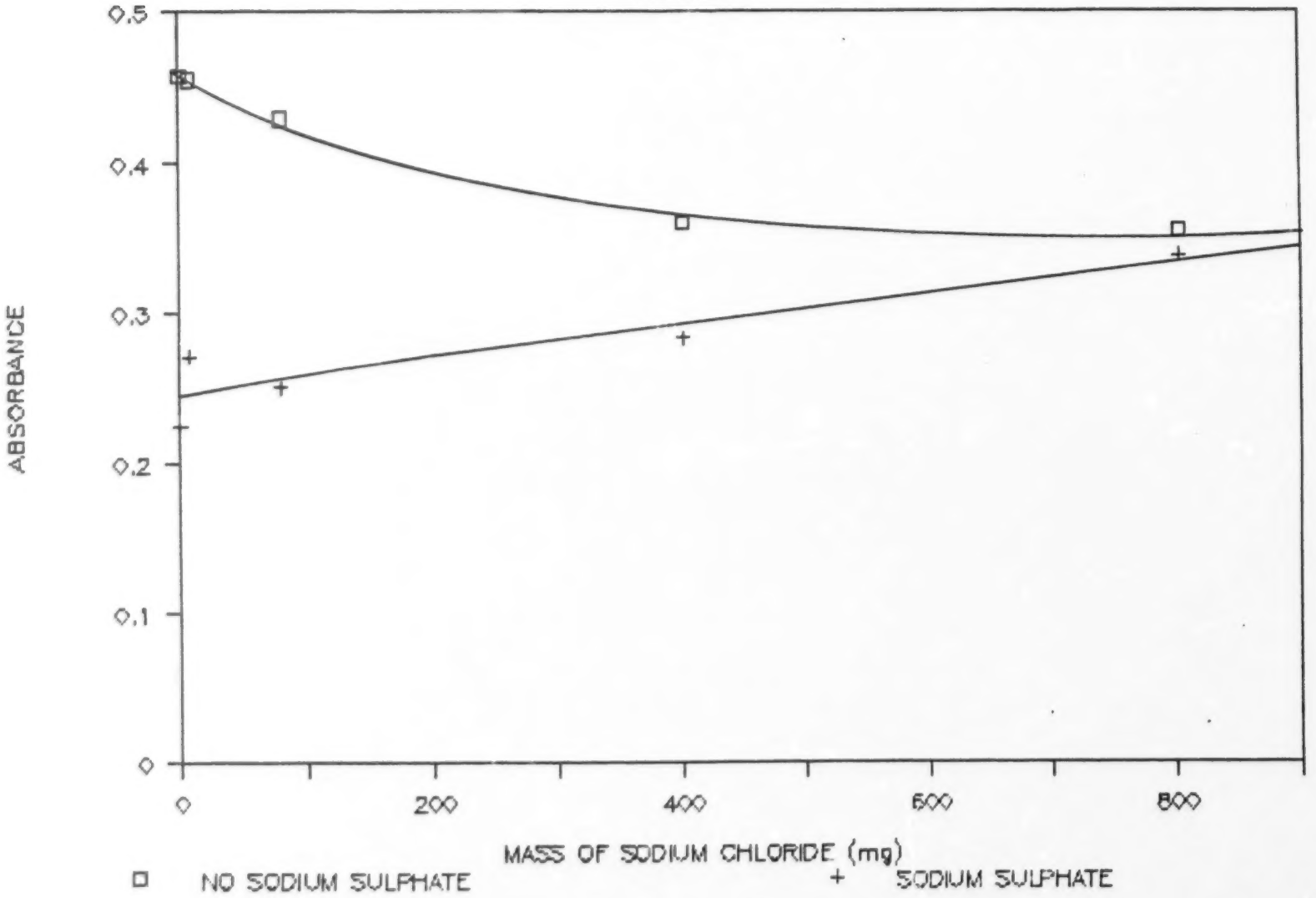
PART II

EFFECT OF SODIUM CHLORIDE
Figure 17

Mass of Sodium Chloride (mg)	Absorbance	
	Constant Ionic Strength	Standard Conditions
0.0	0.225	0.457
8.0	0.271	0.455
80.4	0.250	0.429
401.8	0.283	0.360
803.6	0.338	0.355
Experimental Conditions:		
Experiment #	STI 34	STI 33
Final Volume	46 ml	46 ml
Dry Mass PAM	148 ug	148 ug
Mass Sodium Sulphate	3.4 g	0 g
Path Length	1 cm	1 cm
Wavelength	610 nm	610 nm

EFFECT OF SODIUM CHLORIDE

FIGURE 17



PART II

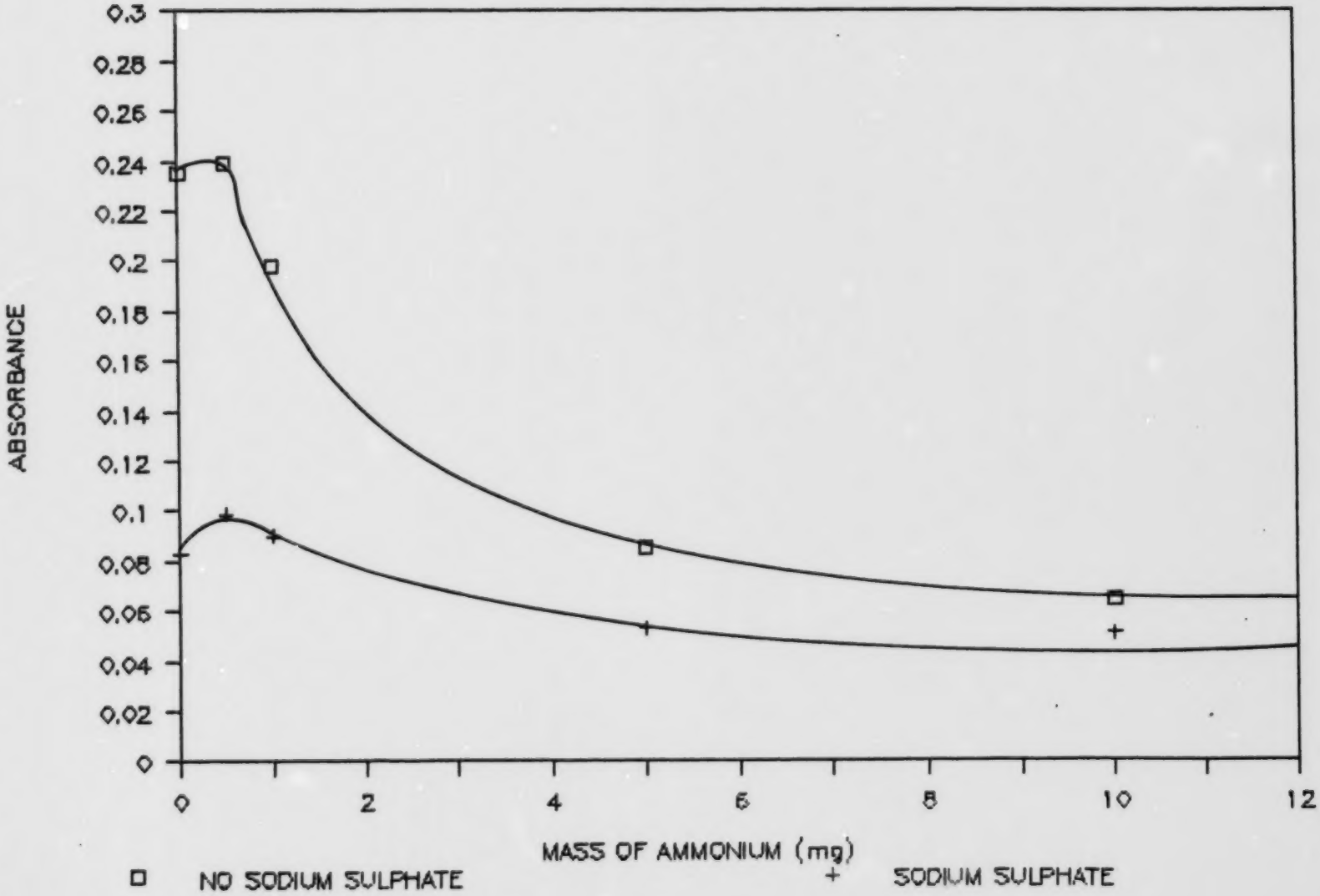
EFFECT OF AMMONIUM
Figure 18

Mass of Ammonium (mg)	Absorbance: Constant Ionic Strength	Absorbance: Standard Conditions
0.0	0.083	0.235
0.5	0.099	0.239
1.0	0.090	0.198
5.0	0.053	0.085
10.0	0.051	0.065

Experimental Conditions:		
Experiment #	STI 47	STI 46
Final Volume	46 ml	46 ml
Dry Mass PAM	126 ug	126 ug
Mass Sodium Sulphate	3.4 g	0 g
Path Length	1 cm	1 cm
Wavelength	610 nm	610 nm

EFFECT OF AMMONIUM

FIGURE 18



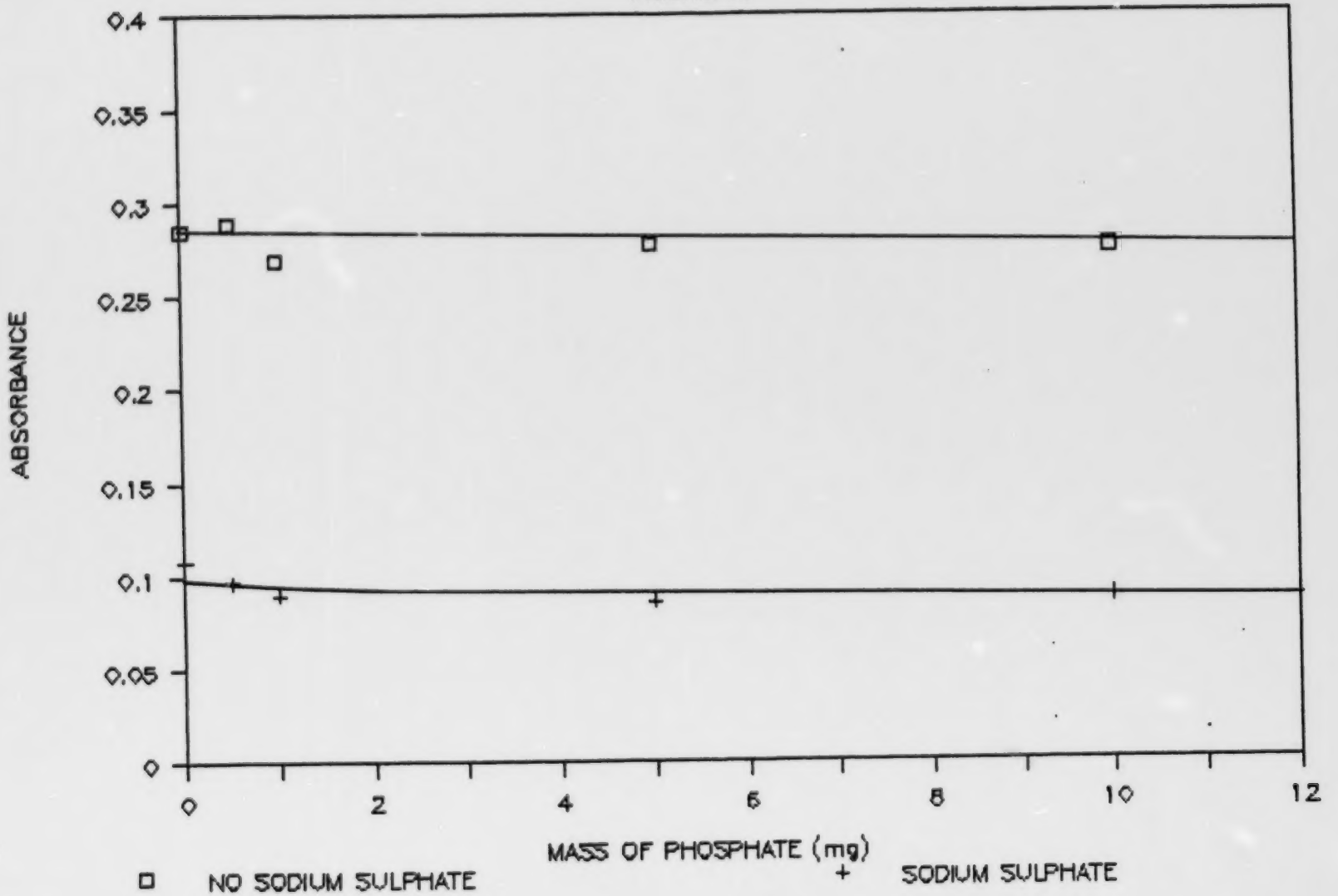
PART II

EFFECT OF PHOSPHATE
Figure 19

Mass of Phosphate (mg)	Absorbance	
	Constant Ionic Strength	Standard Conditions
0.0	0.108	0.285
0.5	0.097	0.289
1.0	0.090	0.269
5.0	0.086	0.277
10.0	0.088	0.275
Experimental Conditions:		
Experiment #	STI 41	STI 40
Final Volume	46 ml	46 ml
Dry Mass PAM	126 ug	126 ug
Mass Sodium Sulphate	3.4 g	0 g
Path Length	1 cm	1 cm
Wavelength	610 nm	610 nm

EFFECT OF PHOSPHATE

FIGURE 19



PART II

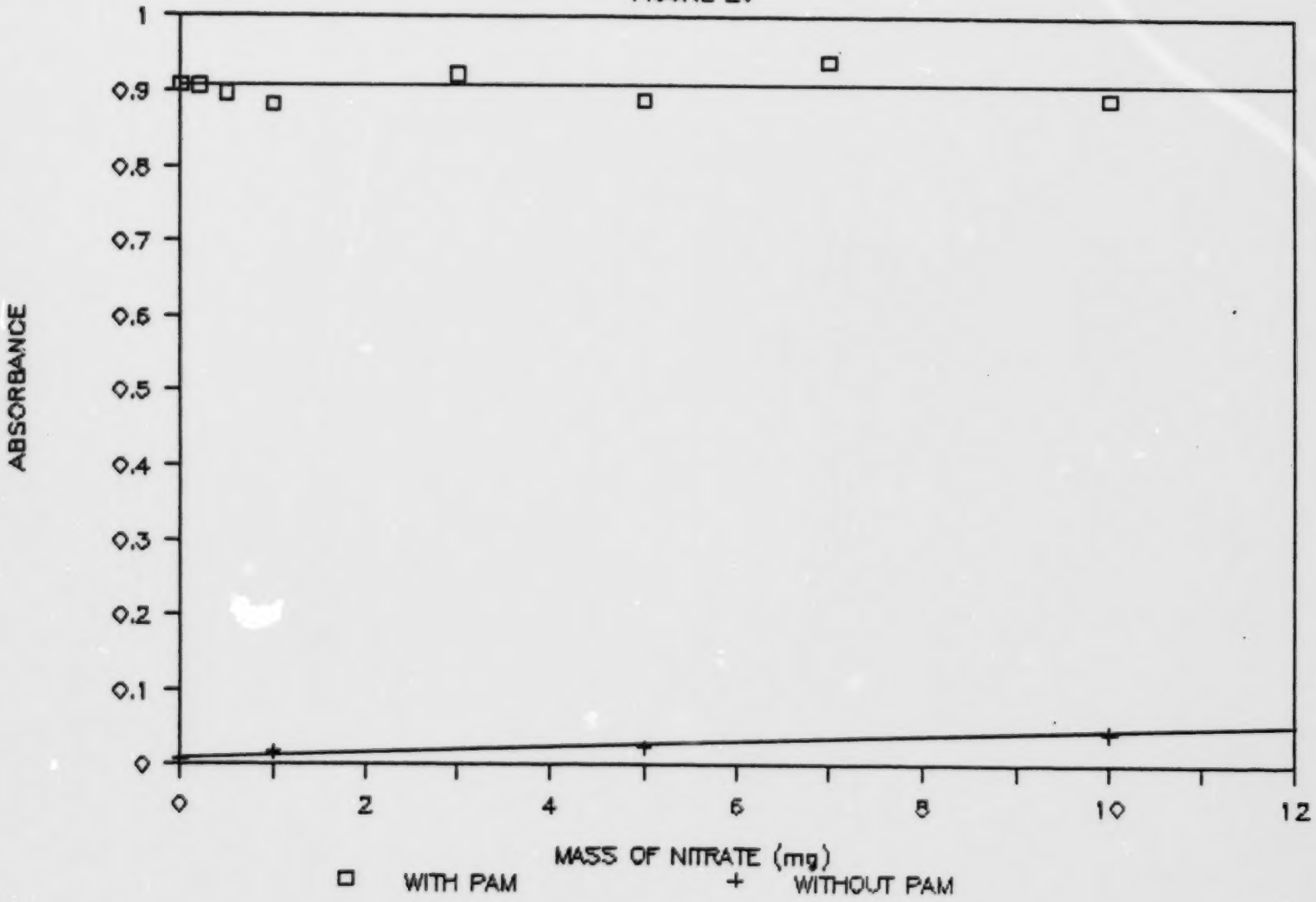
EFFECT OF NITRATE
Figure 20

Mass of Nitrate (mg)	Absorbance	
	Constant PAM	Without PAM
0.0	0.908	0.008
0.2	0.907	1000
0.5	0.897	1000
1.0	0.883	0.017
3.0	0.923	1000
5.0	0.890	0.023
7.0	0.942	1000
10.0	0.893	0.044
Experimental Conditions:		
Experiment #	STI 75	STI 76
Final Volume	46 ml	46 ml
Dry Mass PAM	218 ug	0 ug
Mass Sodium Sulphate	0 g	0 g
Path Length	1 cm	1 cm
Wavelength	610 nm	610 nm

NOTE: When an absorbance value was not obtained for a given mass of nitrate, an arbitrary absorbance value of 1000 was entered in the table.

EFFECT OF NITRATE

FIGURE 20



PART II

IODIDE EFFECT;
WITHOUT PAM
Figure 21

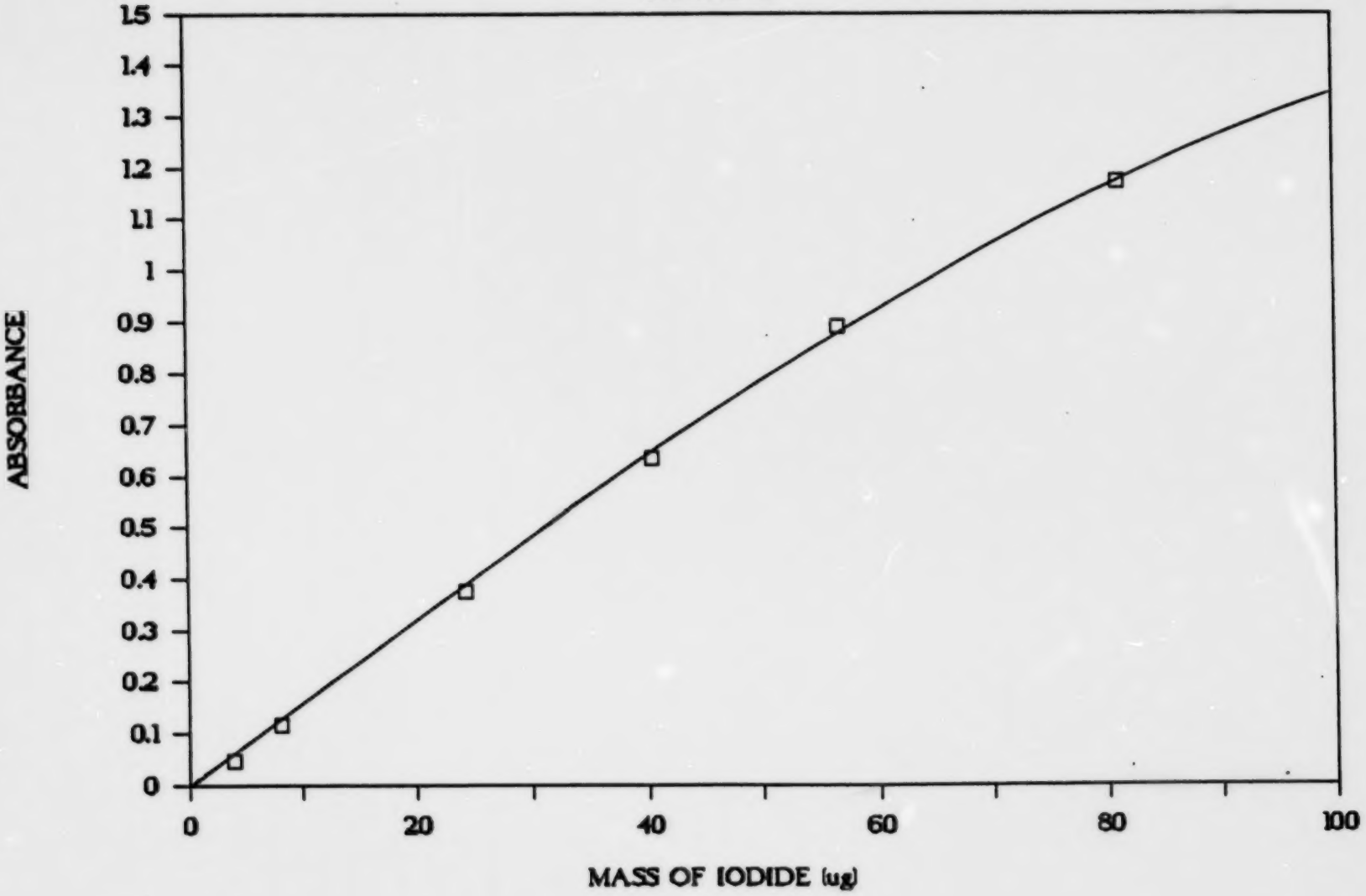
Mass of Iodide (ug)	Absorbance
4.0	0.049
8.1	0.117
24.3	0.377
40.5	0.635
56.7	0.890
81.1	1.173

Experimental Conditions:

Experiment #.....	STI 42
Final Volume.....	46 ml
Dry Mass PAM.....	0 ug
Mass Sodium Sulphate.....	0 g
Path Length.....	1 cm
Wavelength.....	610 nm

IODIDE EFFECT: WITHOUT PAM

FIGURE 21



PART II

IODIDE EFFECT;
SODIUM SULPHATE, NO PAM
Figure 22

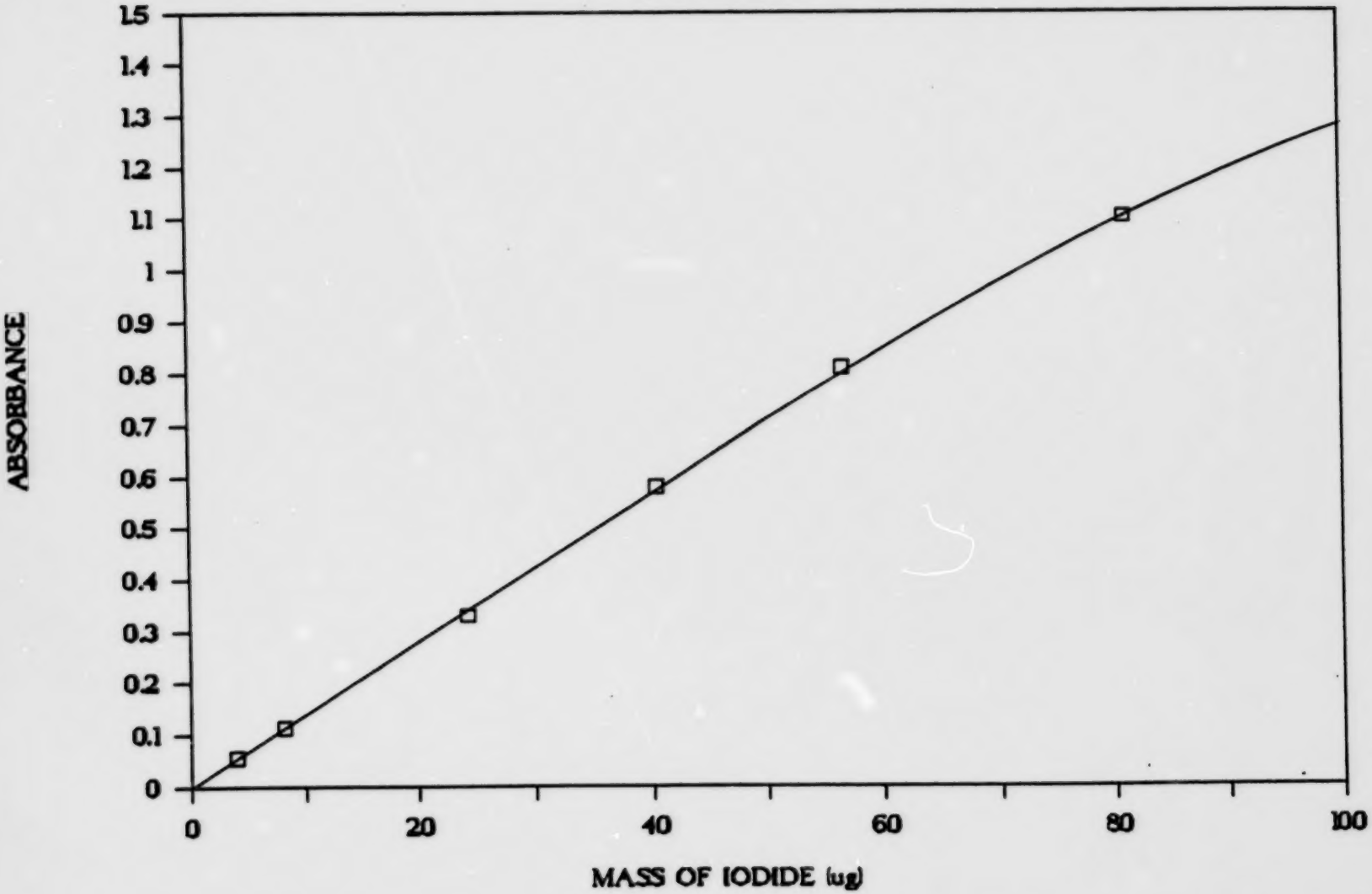
Mass of Iodide (ug)	Absorbance
4.0	0.056
8.1	0.113
24.3	0.331
40.5	0.579
56.7	0.809
81.1	1.102

Experimental Conditions:

Experiment #.....	STI 43
Final Volume.....	46 ml
Dry Mass PAM.....	0 ug
Mass Sodium Sulphate.....	3.4 g
Path Length.....	1 cm
Wavelength.....	610 nm

IODIDE EFFECT: SODIUM SULPHATE, NO PAM

FIGURE 22



PART II

PHENOL EFFECT;
WITHOUT PAM
Figure 23

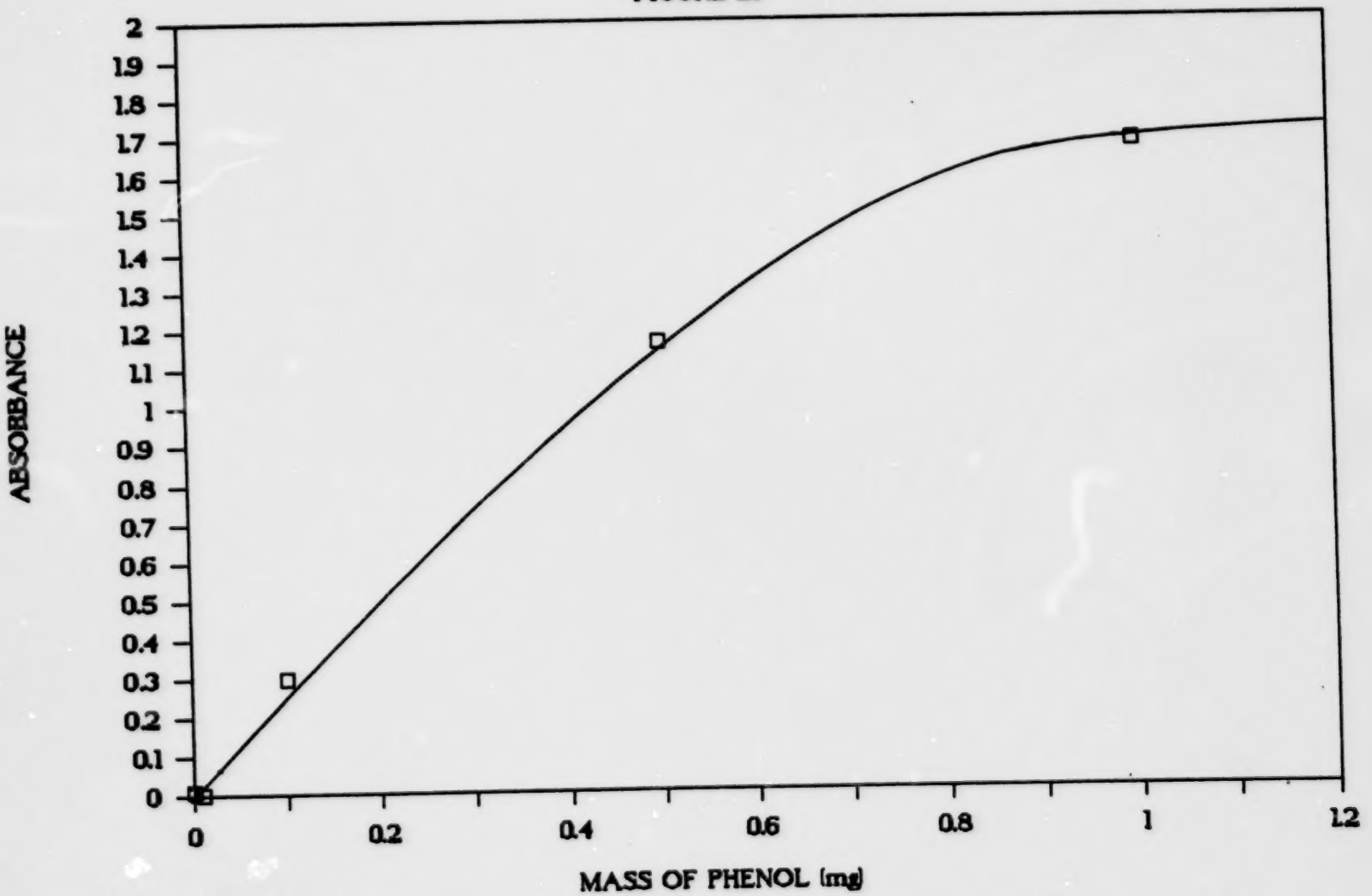
Mass of Phenol (mg)	Absorbance
0.001	0.009
0.010	0.002
0.100	0.297
0.500	1.163
1.000	1.679

Experimental Conditions:

Experiment #.....	STI 52
Final Volume.....	46 ml
Dry Mass PAM.....	0 ug
Mass Sodium Sulphate.....	0 g
Path Length.....	1 cm
Wavelength.....	610 nm

PHENOL EFFECT: WITHOUT PAM

FIGURE 23



PART II

PHENOL EFFECT;
WITHOUT PAM
Figure 24

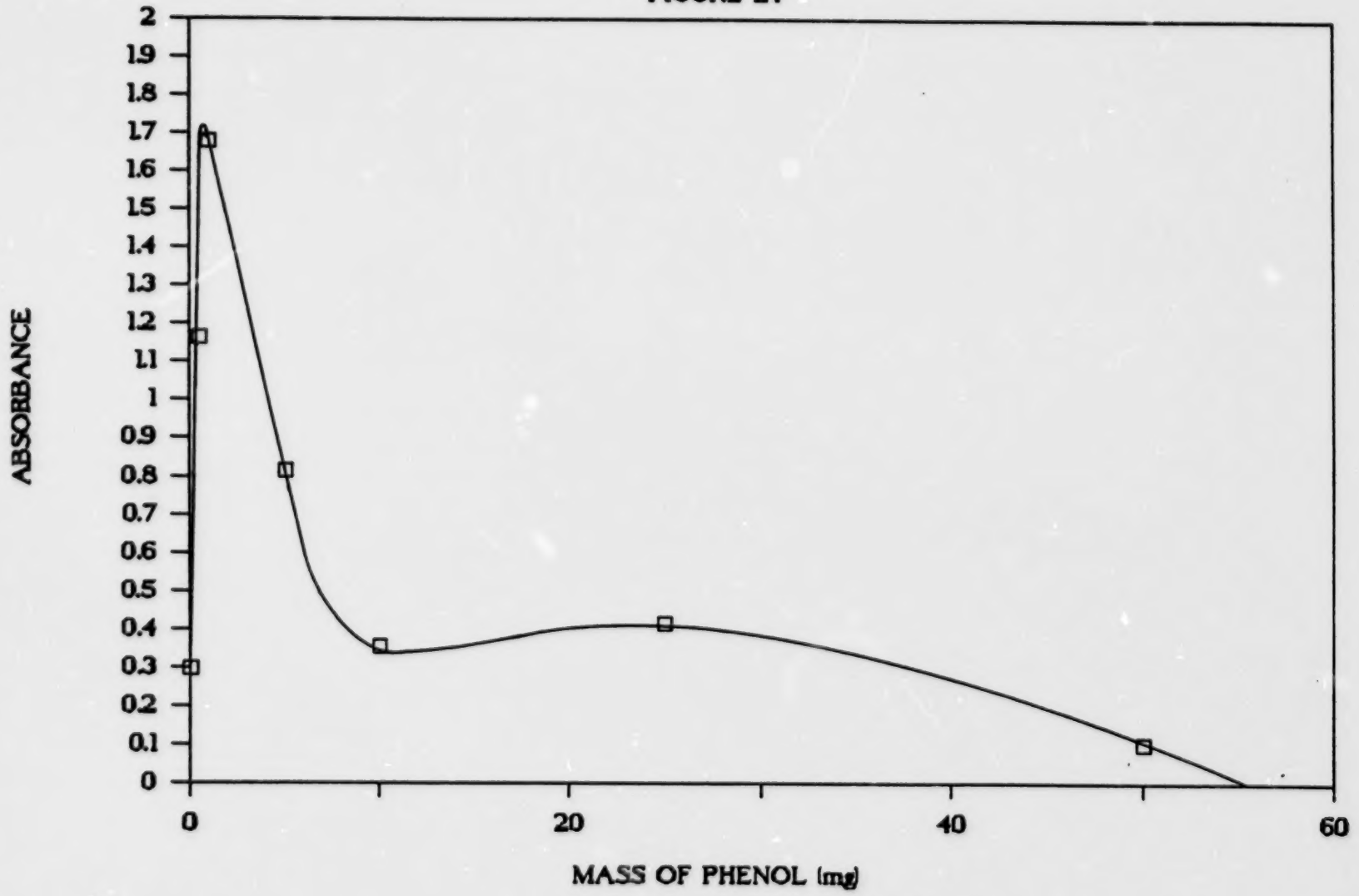
Mass of Phenol (mg)	Absorbance
0.1	0.297
0.5	1.163
1.0	1.679
5.0	0.815
10.0	0.356
25	0.417
50	0.101

Experimental Conditions:

Experiment #.....	STI 52
Final Volume.....	46 ml
Dry Mass PAM.....	0 ug
Mass Sodium Sulphate.....	0 g
Path Length.....	1 cm
Wavelength.....	610 nm

PHENOL EFFECT: WITHOUT PAM

FIGURE 24



PART II

EFFECT OF ACETONE
Figure 25

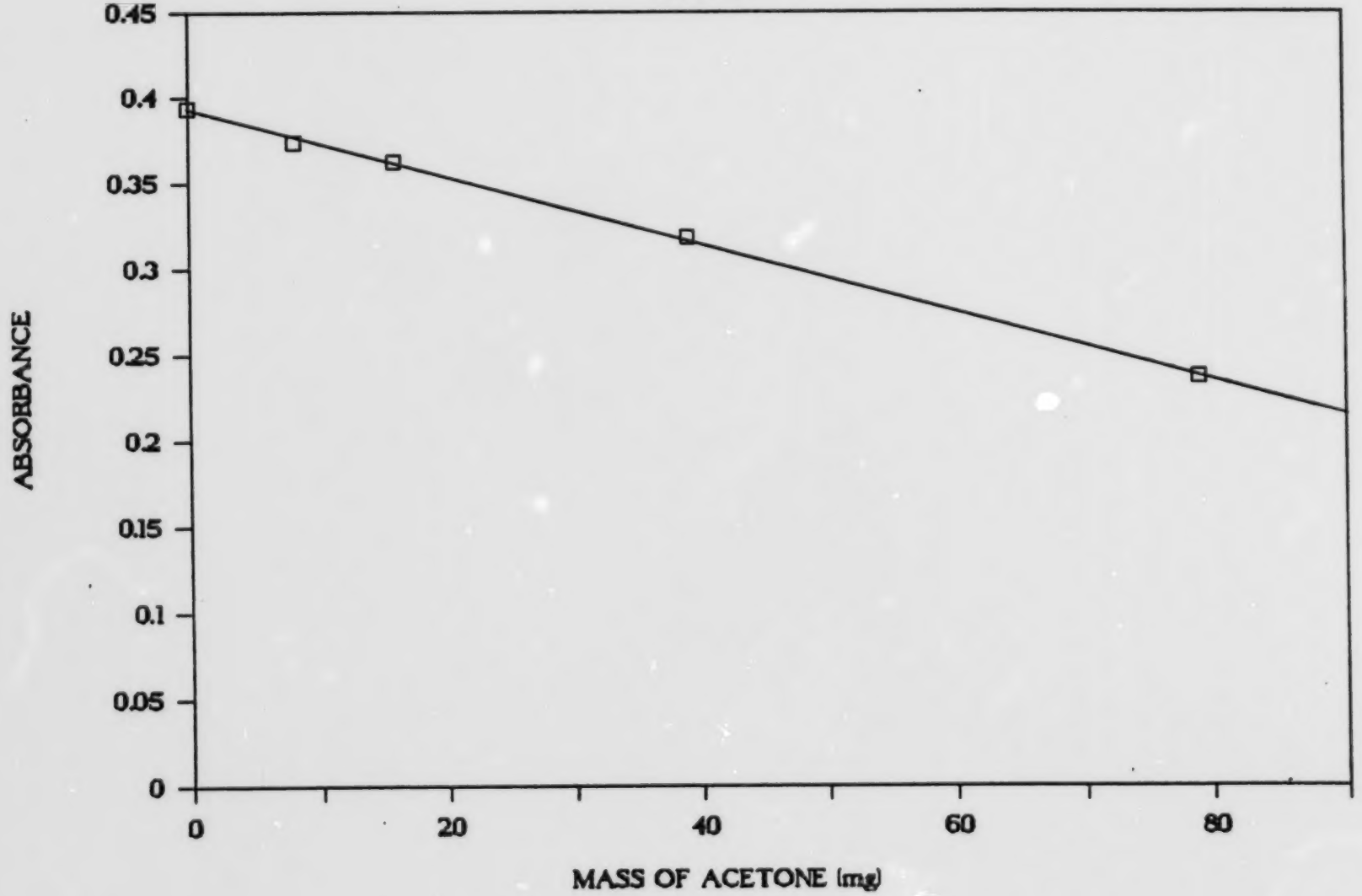
Mass of Acetone (mg)	Absorbance
0.0	0.394
7.9	0.374
15.8	0.363
39.5	0.319
79.0	0.238

Experimental Conditions:

Experiment #.....	STI 54
Final Volume.....	46 ml
Dry Mass PAM.....	129 ug
Mass Sodium Sulphate.....	0 g
Path Length.....	1 cm
Wavelength.....	610 nm

EFFECT OF ACETONE

FIGURE 25



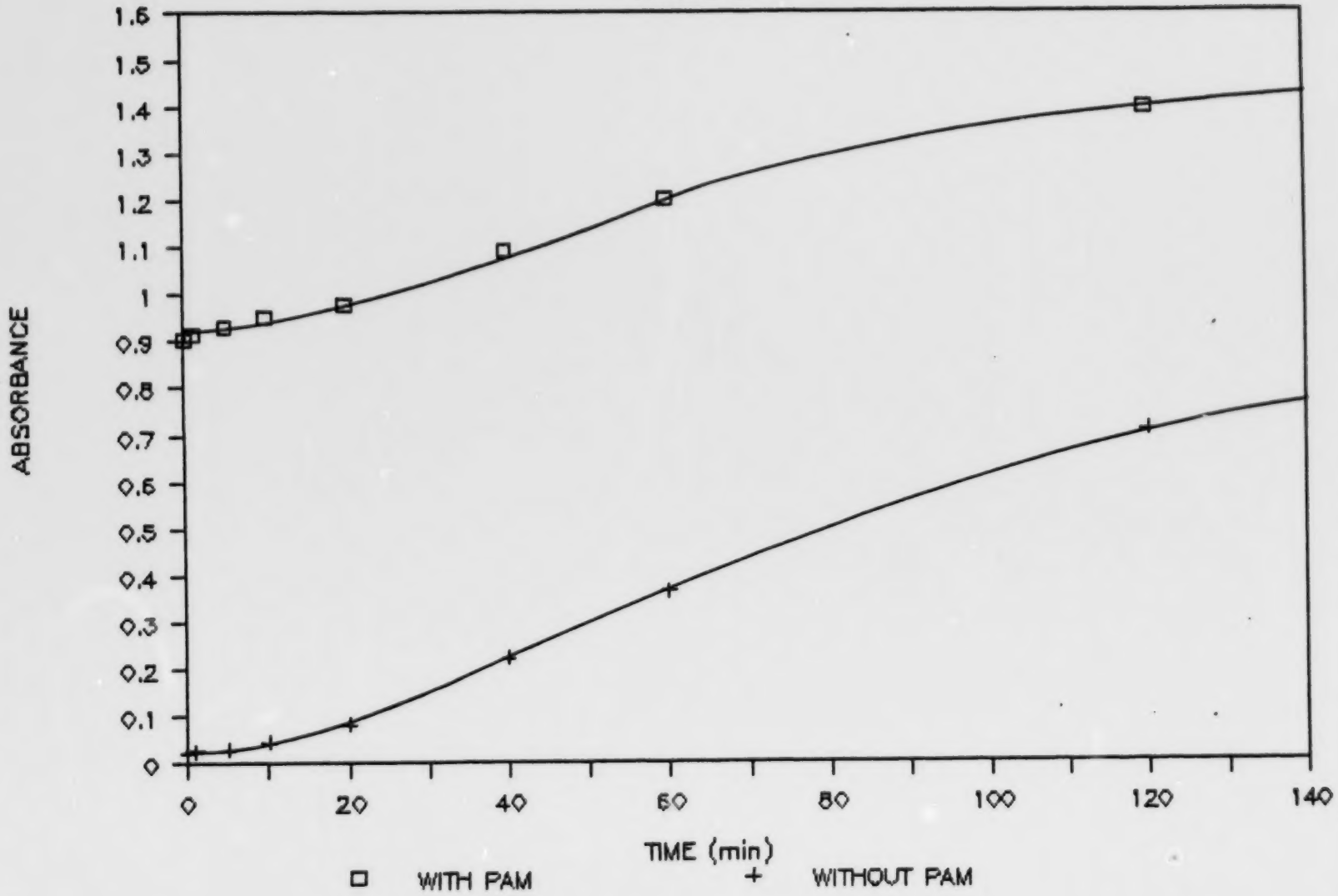
PART II

EFFECT OF MALEIC ACID OVER TIME
Figure 26

Time of Reaction (min)	Absorbance	
	Constant PAM	Without PAM
0	0.904	0.024
1	0.914	0.027
5	0.931	0.031
10	0.95	0.045
20	0.976	0.083
40	1.094	0.224
60	1.204	0.368
120	1.398	0.71
Experimental Conditions:		
Experiment #	STI 74	STI 74
Final Volume	46 ml	46 ml
Dry Mass PAM	219 ug	0 ug
Mass Sodium Sulphate	0 g	0 g
Path Length	1 cm	1 cm
Wavelength	610 nm	610 nm

EFFECT OF MALEIC ACID OVER TIME

FIGURE 26



PART II

EFFECT OF MALEIC ACID
Figure 27

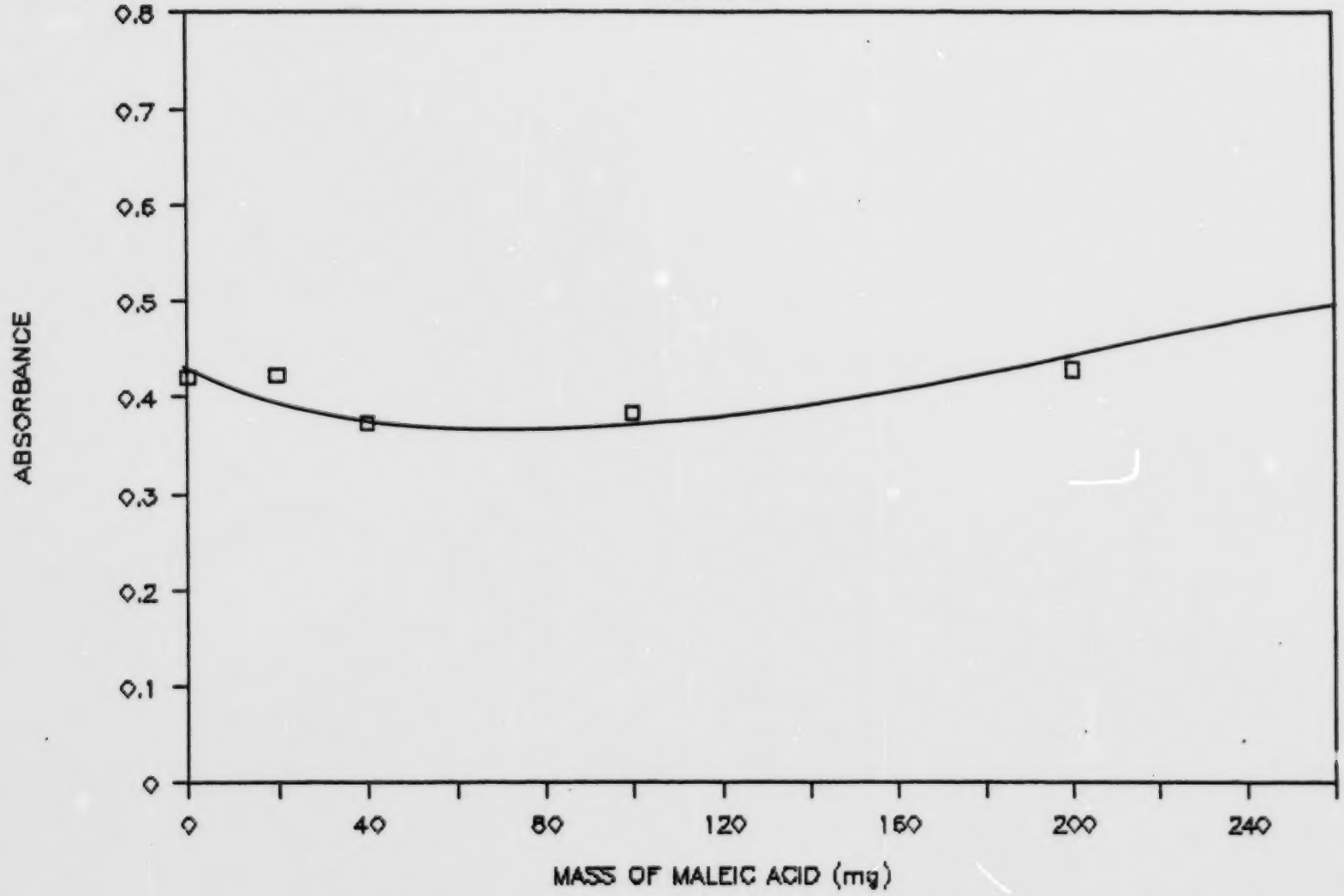
Mass of Maleic acid (mg)	Absorbance
0	0.420
20	0.423
40	0.373
100	0.384
200	0.430

Experimental Conditions:

Experiment #.....	STI 59
Final Volume.....	46 ml
Dry Mass PAM.....	129 ug
Mass Sodium Sulphate.....	0 g
Path Length.....	1 cm
Wavelength.....	610 nm

EFFECT OF MALEIC ACID

FIGURE 27



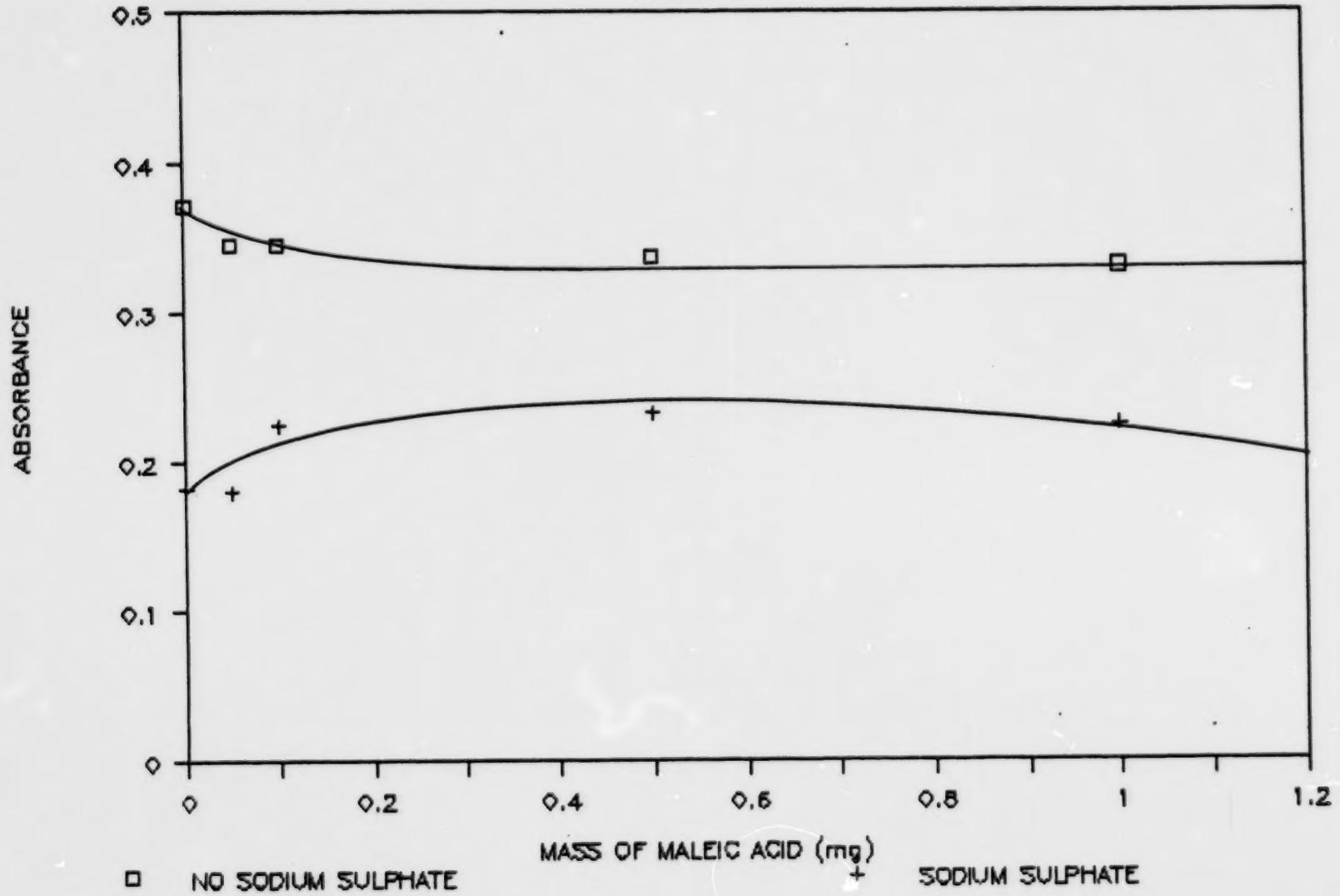
PART II

EFFECT OF MALEIC ACID
Figure 28

Mass of Maleic Acid (mg)	Absorbance: Constant Ionic Strength	Absorbance: Standard Conditions
0.00	0.183	0.371
0.05	0.180	0.345
0.10	0.224	0.344
0.50	0.232	0.337
1.00	0.225	0.331
Experimental Conditions:		
Experiment #	STI 62	STI 61
Final Volume	46 ml	46 ml
Dry Mass PAM	129 ug	129 ug
Mass Sodium Sulphate	3.4 g	0 g
Path Length	1 cm	1 cm
Wavelength	610 nm	610 nm

EFFECT OF MALEIC ACID

FIGURE 28



PART II

HUMIC ACID EFFECT;
WITHOUT PAM
Figure 29

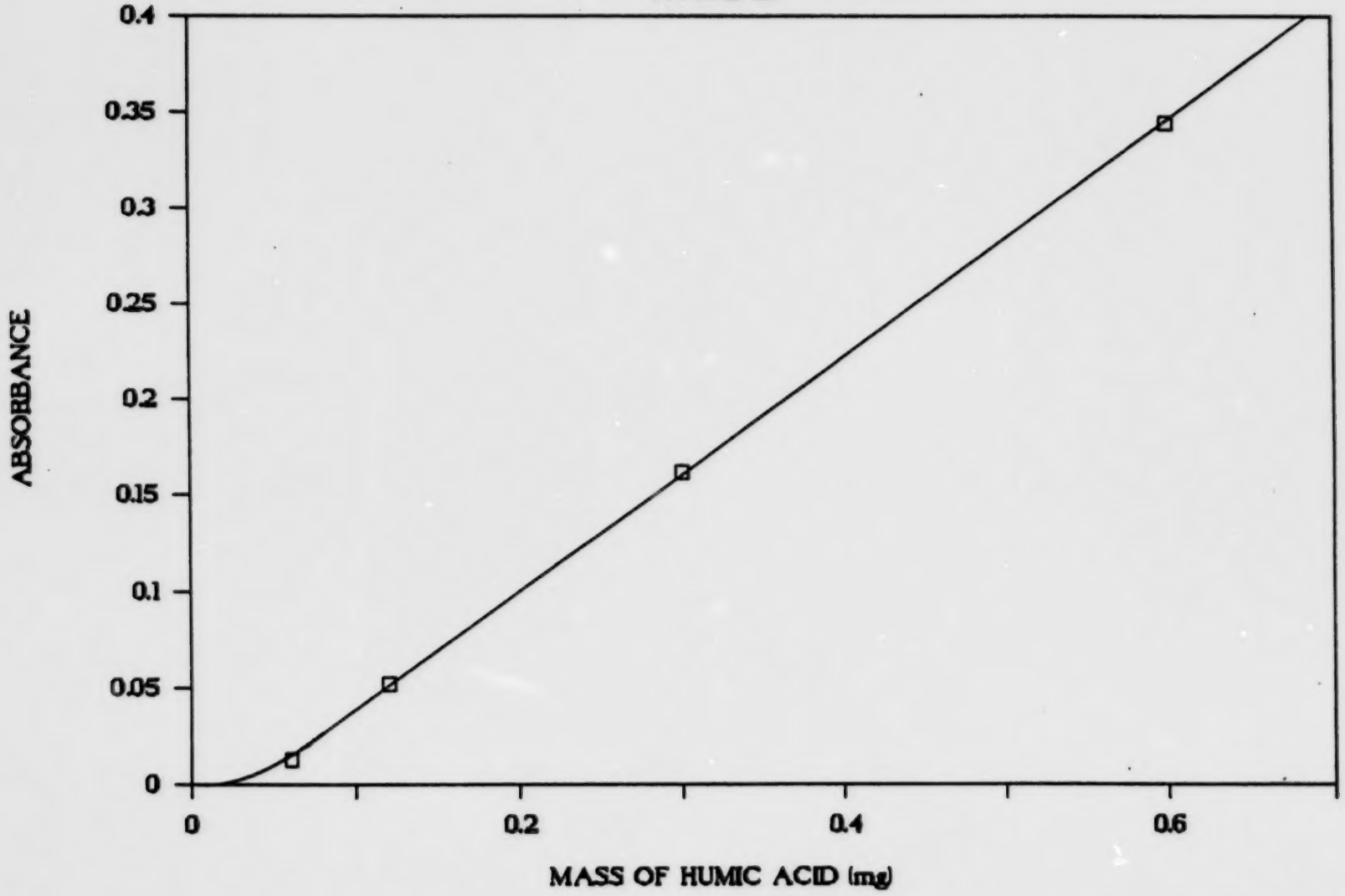
Mass of Humic acid (mg)	Absorbance
0.06	0.013
0.12	0.052
0.30	0.162
0.60	0.344

Experimental Conditions:

Experiment #.....	STI 64
Final Volume.....	46 ml
Dry Mass PAM.....	0 ug
Mass Sodium Sulphate.....	0 g
Path Length.....	1 cm
Wavelength.....	610 nm

HUMIC ACID EFFECT: WITHOUT PAM

FIGURE 29



PART II

EFFECT OF OIL
Figure 30

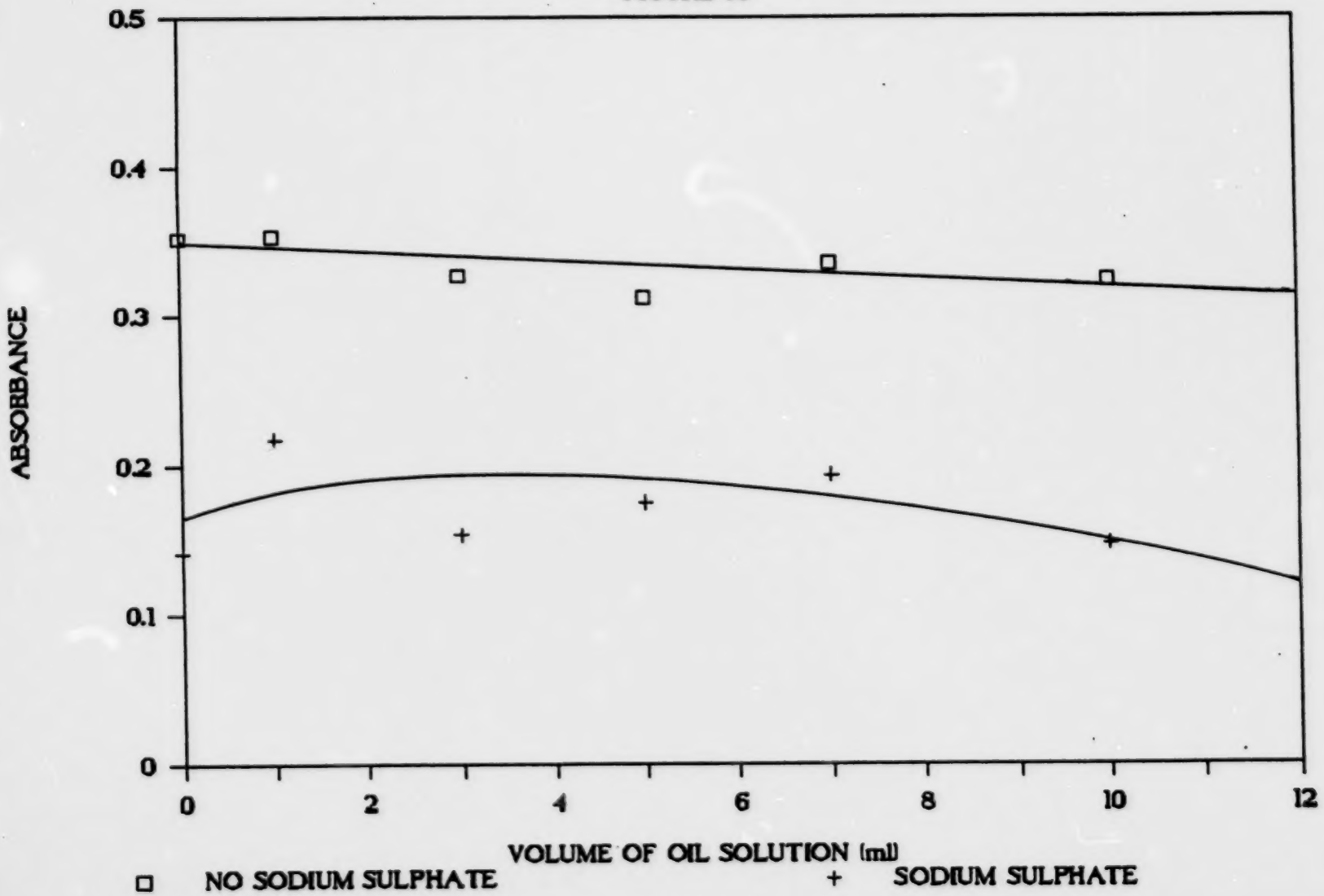
Volume of Saturated Oil Solution (ml)	Absorbances			
	Constant Ionic Strength		Standard Conditions	
	Abs	Abs-Blk *	Abs	Abs-Blk *
0	0.213	0.141	0.354	0.352
1	0.225	0.217	0.361	0.353
3	0.234	0.153	0.350	0.327
5	0.247	0.175	0.351	0.313
7	0.265	0.193	0.388	0.335
10	0.222	0.147	0.400	0.324

Experimental Conditions:		
Experiment #	STI 68	STI 67
Final Volume	46 ml	46 ml
Reagent Blank Absorbance	0.072	0.002
Dry Mass PAM	129 ug	129 ug
Mass Sodium Sulphate	3.4 g	0 g
Path Length	1 cm	1 cm
Wavelength	610 nm	610 nm

* Sample blank and reagent blank were subtracted to account for turbidity and reagent absorbance, respectively.

EFFECT OF OIL

FIGURE 30

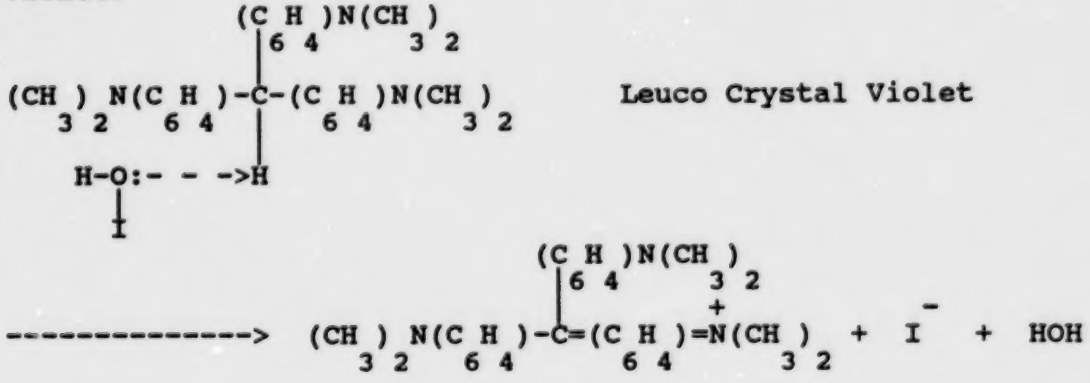


PART III

The Leuco Crystal Violet Method

INTRODUCTION

The leuco crystal violet method for the determination of polyacrylamide (PAM) in water, was derived by combining the triiodide procedure for PAM determination (1) with the leuco crystal violet method for the determination of iodine (2). Triiodide ion is developed from iodide and brominated PAM by the same mechanism as the triiodide method (1) described in Part I of this series. Rather than directly reading the absorbance of triiodide in the ultraviolet range, triiodide was reacted with mercuric chloride to form hypoiodous acid . Hypoiodous acid in turn, reacted with leuco crystal violet to form crystal violet dye. Black and Whittle (3) proposed a hydride transfer mechanism for the oxidation of leuco crystal violet:



Crystal Violet Dye

The blue colour of crystal violet dye absorbs at a wavelength of 592 nm in the visible range where absorption interference from most common organic contaminants is negligible. Hence, the method has a potential for application to coal water samples.

Since the triiodide method for the determination of PAM and the leuco crystal violet method for iodine determination have not been applied together, mutually favourable conditions were required. Therefore, it was necessary for method development experimentation before the effect of common contaminants in coal water could be studied. Once this was accomplished, several organic, cationic and anionic contaminants were introduced into the adopted method in order to observe their effects.

EXPERIMENTAL

Reagents and Apparatus

Anionic Dow Separan MG 700 was used as standard polyacrylamide (PAM). Stock solutions were prepared by accurately weighing 70 to 80 mg of PAM into a 500 ml volumetric flask and wetting the polymer with 1 ml of methanol before diluting to volume with distilled water. A 100 ml aliquot of the stock solution was diluted to 250 ml for the standard 55 to 66 ppm PAM solution. The actual PAM concentration was calculated by accounting for percent moisture in the PAM. Both stock and standard PAM solutions were shaken or stirred for at least 3 hours prior to use. Stock solutions were stable for more than 6 months where as standards would loose strength in one to two weeks.

The buffer solution was prepared to maintain a pH of 3.7. 19.0 g of anhydrous sodium acetate was dissolved in 103 ml of glacial acetic acid and diluted to 1000 ml with distilled water. The pH was adjusted to 3.7 with 50 % acetic acid.

Leuco crystal violet indicator was obtained from Aldrich (catalogue # 21-921-5). 1.5 g of indicator was added, with stirring, to approximately 200 ml of a 16 ml/l sulfuric acid solution. The indicator was washed down the sides of the container with distilled water and stirring was continued until dissolution was completed. 800 ml of a 3.125 g/l solution of $HgCl_2$ was then introduced into the indicator

solution while maintaining stirring. The pH of the solution was adjusted to below 1.5 with concentrated H_2SO_4 added drop-wise. The final solution was stored in a brown glass bottle at 8 ^{o}C and was discarded after 6 months.

Other reagents included: a 10 g/l sodium formate solution (prepared weekly), saturated bromine water (prepared daily) and a 1.31 g/l potassium iodide solution which was discarded when it turned yellow. All the reagents were used to determine the sensitivity of the optimum method and study the effect of interferences. Variations of the reagent concentrations were used to develop the final optimum method.

Absorbance measurements were made on a Beckman Acta III Spectrophotometer at a wavelength of 592 nm in 1 cm quartz cells. Elemental analysis of the PAM standard polymer was performed on a Perkin-Elmer Model 240 Elemental Analyser, and a Varian Techtron Atomic Absorption Spectrophotometer.

Procedure

Determination of a standard curve was accomplished by preparing aliquots from 0.2 to 15 ml of standard PAM solution in 50 ml graduated test tubes. The solutions were diluted to 35 ml with distilled water and reagents were introduced with shaking after each addition. The standards were brominated with 1 ml of saturated bromine water and then were allowed to sit for 15 minutes. Excess bromine was destroyed with 5 ml of sodium formate solution and the solutions were left to sit

another 5 minutes. One ml of potassium iodide and one ml of leuco crystal violet solutions were added and the standards were diluted to 50 ml. Each standard was read spectrophotometrically after 20 minutes at a wavelength of 592 nm in 1 cm quartz cells with a distilled water reference. A standard curve of absorbance versus ug of PAM was plotted from the resulting measurements.

The optimum conditions for the method were derived by following the same procedure used for the PAM curves except with constant PAM mass and varied aliquots of reagent. Applying this to potassium iodide was straight forward, but, determination of the optimum pH required adjustments of the pH after the addition of each reagent. At the point in the procedure reserved for buffer addition, aliquots of 3 N HCl or 1 N NaOH and 33 % NaOH were added to achieve the desired pH. As each reagent was added, the pH was monitered and adjusted in order to maintain the pH. Adjustments were required more in the basic range than in the acidic range especially after bromination.

Determination of the effect of contaminants was accomplished by adding aliquots of a solution of contaminant to a series of PAM standards of equal mass (usually around 210 ug PAM). Reagents were added according to the general procedure and plots of absorbance versus compound or ion mass were produced. These experiments were repeated under constant ionic strength conditions by adding 5 ml of a 100 g/l

solution of sodium sulphate to the samples before reagent addition. Those interferences with a positive effect on colour intensity were further examined in the absence of PAM. From these experiments the nature of the interference, if any, was determined for a particular compound or ion.

DISCUSSION AND RESULTS

Experiments were designed to derive the method conditions that would provide optimum results and to examine the effects on the method of contaminants typically found in coal wash waters. Parameters considered in the optimisation of the method were linearity, sensitivity and stability of the developed colour. Contaminants where studied to determine the nature, cause and mass range of their effects on the method.

Results of analysis on DOW Separan MG 700 polymer are in Table 1. The percentage of acrylamide groups on the polymer was proportional to colour development in the leuco crystal violet method due to the availability of amide groups for bromination. Details of the method for acrylamide group determination are in Appendix 1 at the end of this series.

TABLE 1

ANALYSIS OF DOW SEPARAN MG 700

Carbon	41.07 % of dry mass
Hydrogen	5.37 % of dry mass
Nitrogen	11.04 % of dry mass
Sodium	12.18 % of dry mass
Oxygen	29.89 % of dry mass
Ash	24.6 % of dry mass
Acrylamide	49.0 % of dry mass
Moisture	13.1 % of total mass

Optimisation of the Method

Acidic conditions were chosen because of practical application to the leuco crystal violet method and minimal interference. Maximum colour development, under constant PAM conditions, occured in the pH range from 3.9 to 5.5 (Fig. 1). A second peak in absorbance was observed at pH 7. High absorbances were also observed greater than pH 7. However, in order to maintain pH 7 or higher, the method required pH adjustments throughout the procedure due to HBr formation after PAM bromination and destruction of excess bromine. Even the highest capacity buffers could not maintain neutrality or alkalinity after polyacrylamide bromination. Also, alkalinity itself consumed bromine by pulling the following equilibriums to the right:

$$2Br_2 + 2HOH = 4H^+ + 4Br^- + O_2 \qquad Br_2 + HOH = H^+ + Br^- + HOBr$$

Therefore, only acidic conditions were practical for the method.

The buffer type was chosen on the basis of maximum sensitivity and minimum interference. Acetate buffer produced similar peak absorbances as in Figure 1, but high blanks were obtained for pH greater than 3.8. Citrate buffer produced peak absorbances in the range from pH 5.0 to 5.7 but a precipitate formed for pH greater than 4.0. The optimum compromise between maximum sensitivity and minimum additive interference was at pH 3.7 for acetate buffer and pH 3.9 for citrate buffer.

The performance of acetate buffer was superior to citrate buffer in terms of linearity, sensitivity and time stability of the developed colour (Fig. 2). Both buffers were initially linear with over 500 ug of PAM. Citrate buffer, however, lost linearity after 20 hours. Acetate buffer remained linear even though 15 % of the original absorbance was lost. In terms of sensitivity, the method with acetate buffer could detect one fifth the mass of PAM than the method with citrate buffer.

The amount of potassium iodide reagent affected sensitivity and blank values. The best compromise between high sensitivity and low blank absorbances was accomplished with 1.3 mg of KI reagent added (Fig. 3). Potassium iodide in excess of 75 ppm also produced a precipitate in the presence of 43 ppm of leuco crystal violet reagent.

The age of sodium formate reagent solution had an effect on the method sensitivity. A two week old sodium formate solution had the potential to decrease absorbances by 50 % of absorbances developed with freshly prepared reagent.

The optimum reaction times for the bromination step and the reduction of excess bromine were not studied in detail, however, the method was not very time dependant overall. Scoggins (4) found that a 15 to 40 minute bromination period and five minute reduction time produced maximum absorbance

values for PAM determination by the starch-triiodide method. The blank absorbances doubled within 25 minutes of leuco crystal violet indicator addition but the net effect on the standard curve was minimal. The best results were obtained when the absorbance was read 20 minutes after the addition of the indicator reagent.

The leuco crystal violet method, applied under optimum conditions, was sensitive to 0.5 ug of PAM*. The method was linear over 600 ug of PAM and remained linear for over 20 hours. The standard curve (Fig. 4) had a correlation coefficient (r^2) of 0.999 and a blank value of 0.030 absorbance units. The average inverse slope for standard curves that were generated on separate occasions was 497 ug of PAM per absorbance (N=6). The standard deviation was 6 % or 31 ug of PAM per absorbance, hence, the standard curves were fairly reproducible. Nevertheless, new curves were generated for each set of analysis especially when new reagents were used. Under constant ionic strength conditions, the linearity remained unchanged, but, the sensitivity was affected with PAM detectable to 0.6 ug.

Effect of Ionic Strength

Ionic strength was studied with sodium sulphate. The result under constant PAM concentration was a negative influence on

---

* Amount of PAM, in the final volume, required to give an absorbance of 0.001 units when measured in 1 cm cells.

colour development (Fig. 5). This effect was observed with more than 0.01 g of Na_2SO_4. A constant negative interference dropped the absorbance 10 % of the original in the range from 0.2 g to 1 g Na_2SO_4. In the absence of PAM, no contribution to the absorbance was observed above the blank value. Over 1 g of Na_2SO_4 caused inconsistent absorbance results.

The double charge on sulphate made it useful as an ionic strength buffer, assuming that this was the only factor contributing to its effect. Ionic strength was held constant by introduction of a known excess amount of sodium sulphate into the procedure. The cause of the interference was attributed to ionic strength, if its effects were observed under normal conditions but not under constant ionic strength. The standard curve for the leuco crystal violet method under constant ionic strength was less sensitive than under normal conditions, however, it remained linear for over 600 ug of PAM (Fig. 4).

Effect of Divalent Metallic Ions

Divalent calcium was studied as its nitrate while magnesium and zinc were studied as sulphates. Magnesium and zinc were introduced in quantities low enough for sulphate to have a negligible effect. Zinc did not influence the method when present below 10 mg Zn^{2+} and possibly higher (Fig. 6). Magnesium lowers absorbance results by 10 % when greater than

5 mg due to ionic strength interference. The influence of Mg^{2+} can be seen with as little as 1 mg (Fig. 7).

Calcium nitrate caused high absorbances when present over 0.01 mg (Fig. 8). Greater than 1 mg of $Ca(NO_3)_2$ produced inconsistent results, however, there was a decreasing trend in absorbances. In the high range of $Ca(NO_3)_2$ and under constant ionic strength conditions, the opposite trend was observed (Fig. 9). This result suggested that a negative ionic strength effect was competing with an interference that increased the absorbance. The examination of nitrate's influence on the method (discussed later in the report) revealed that NO_3^- was responsible for the high results. Hence, the hinderance of colour development due to ionic strength was due mostly to divalent calcium.

Less than 10 mg of divalent iron, as its sulphate, seemed to have relatively little effect on the method in the presence of PAM (Fig. 10). Further examination under constant ionic strength conditions revealed a slight increase in absorbance for ferrous ion greater than 0.5 mg. This was observed to a greater extent in the absence of PAM (Fig. 10*). These results inferred that competing positive and negative

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* An expired sodium formate solution caused low absorbances for the experiment under standard conditions. Hence, the curve produced under constant ionic strength conditions had higher absorbances. However, comparisons in the trends could still be made.

influences on the absorbance were acting on the method in equal proportion to produce a net null effect.

The positive interference of ferrous ion was observed visually in the solutions in the form of an orange-brown colour that appeared after bromination and persisted after the destruction of excess bromine. The colour was characteristic of ferric bromide (5) suggesting the presence of Fe^{3+}. Ferric ion was confirmed by the development of a dark red colour on the addition of potassium thiocyanate indicator to the procedure after the bromine destruction step. Bromine oxidised ferrous ion to ferric ion in a manner similar to the reaction:

$$Br_2 + 2FeSO_4 + H_2SO_4 \text{ -------> } Fe_2(SO_4)_3 + 2HBr$$

The produced ferric ion reacted with excess bromine to form the orange-brown colour. The same colour was developed by the direct reaction of ferric ion with bromine. It follows from the ferrous/bromine reaction that some of the negative influence on colour development was due to bromine depletion along with ionic strength interference. The net change in the absorbance due to the three effects appeared to be negligible, however, complications could have caused inconsistant absorbances.

Effect of Trivalent Metallic Ions

Greater than 0.01 mg of ferric ion, as its chloride in the presence of PAM, hindered colour development under normal

conditions and caused high absorbances under constant ionic strength (Fig. 11). In the absence of PAM, ferric ion caused high absorbances under both conditions (Fig. 12). The effects were independent of ferric ion concentration when Fe^{3+} was present over 5 mg. The effects of chloride were negligible in this range. This phenomenon was the result of positive colour interference from ferric bromide absorption, competing with the negative influence of bromine depletion and increased ionic strength. The same effects were observed for ferrous ion, however, contrary to Fe^{2+}, the dominant interferences for ferric ion were negative resulting in a net decrease in the final absorbance.

Trivalent aluminium, as the sulphate, enhanced the absorbance developed by 210 ug of PAM by a maximum of 10 % when present in the range from 0.02 to 0.1 mg of Al^{3+} (Fig. 13). Colour development due to Al^{3+} was not observed in the absence of PAM. More than 1 mg of Al^{3+} produced a strong negative ionic strength effect that reduced absorbances as much as 30 % of the original absorbance without Al^{3+} (Fig. 14).

Effect of Other Cations

Examination of ionic strength effects with sodium sulphate disclosed that sodium did not affect the method when present below 3 mg (Fig. 5). Less that 300 mg sodium decreased absorbance by 10 % assuming no influence from sulphate. Since this assumption was drastic, sulphate was held

partially accountable and the effect of sodium was dismissed as minimal at levels below 300 mg of Na^+.

Ammonium was studied as the chloride in the presence of PAM. Chloride displayed only a slight positive influence on absorbance in the region of NH_4Cl mass that was examined (Fig. 15). Therefore, ammonium alone was considered responsible for the net decrease observed in the colour intensity for amounts of ammonium greater that 1 mg (Fig. 16). The high results in the region from 0 to 1 mg ammonium were attributed to the dominance of the chloride influence in a range where the effect of ammonium was low or negligible. Two further observations were loss of bromine's yellow colour after bromination of PAM, that was proportional to ammonium concentration, and persistance of the ammonium effect under constant ionic strength. These observations suggested that reduction of colour development was due to bromine depletion.

Effects of Anions

High results with chloride contamination in amounts less than 30 mg were mentioned in the discussion of ammonium chloride. The positive influence was observed whether PAM was present or not. When over 30 mg of chloride was introduced as the sodium salt, there was a drastic drop in absorbance even under constant ionic strength (Fig. 15). The minimal negative effect of sodium in the sulphate form did not account for the magnitude of the decrease in absorbance with sodium chloride. The interference was attributed to chloride

alone and its origin was other than that of ionic strength.

Phosphate and nitrate where both introduced into the method as their sodium salts in a range where sodium had negligible effects. Phosphate did not affect the method in amounts less than 10 mg (Fig. 17). Nitrate greater than 0.2 mg, however, had a positvie influence on colour intensity independent of the presence of PAM (Fig. 18). The calcium salt of nitrate, discussed earlier, displayed a similar interference (Fig. 8) as sodium nitrate.

Iodide contamination in ug quanties did not alter the method's outcome. Over 0.4 mg of iodide were required to notice colour development in the absence of PAM. The induced absorbance was linear with respect to iodide mass for over 8 mg I^- (Fig. 19). On reaction with bromine, iodide was capable of both direct oxidation to iodine and formation of iodine dibromide by the mechanism (6):

$$2I^- + Br_2 \longrightarrow 2Br^- + I_2$$

$$I_2 + Br_2 \longrightarrow 2IBr$$

$$IBr + Br^- \longrightarrow IBr_2^-$$

The magnitude of iodide interference depended on the extent to which the mechanism proceded to completion and on the potential of iodine dibromide to react with the mercuric chloride-leuco crystal violet reagent.

Effect of Organic Contaminants

Greater than 0.02 mg and less than 3 mg of phenol developed colour in the absence of PAM and supplemented colour intensity in the presence of PAM (Fig. 20). The effect deteriorated with greater than 3 mg of phenol and a white precipitate formed concurrent to the production of 2,4,6-tribromophenol (6):

$$(C_6H_5)OH + 3Br_2 \text{ -------> } (C_6H_2)Br_3OH + HBr$$

Results in the low mass range of phenol contaminant suggested that tribromophenol was responsible for direct oxidation of I^- to iodine which in turn promoted production of crystal violet dye. Tribromophenol is soluble in water only up to 70 ppm (7) or 3.5 mg in the final volume of the method. Hence, when the tribromophenol precipitate formed, the absorbances dropped commensurate with the consumption of bromine by phenol and colour absorbed in the precipitate.

Acetone enhanced colour intensity in the range from 30 mg to 300 mg (Fig. 21) in the presence of PAM, but, colour development was not induced in the absence of PAM. The effect decayed over 300 mg of acetone. Crystal violet dye, formed from the reactions initiated by PAM, was very soluble in acetone and other organic solvents such as methylene chloride and chloroform. The colour enhancement, therefore, was a result of improved solubility. It follows that the sensitivity of the leuco crystal violet method could be improved if the developed colour was extracted into a solvent

insoluble in water, such as methylene chloride.

Results of polyacrylamide analysis, in the presence of maleic acid, were difficult to reproduce. Initial inspection revealed that over 3 mg of maleic acid enhanced colour intensity when 210 ug of PAM were present but developed no colour in the absence of PAM (Fig. 22). Hence, maleic acid catalysed colour development initiated by PAM when present in mg quantities. Bromine consumption was also observed proportional to maleic acid concentration, illustrated by the loss of yellow colour after the bromination step. These events were consistent, however, the magnitude of the enchancement varied from analysis to analysis.

When higher magnitudes of enhancement were observed with 8 mg of maleic acid and 210 ug of PAM, the colour development took about 20 minutes and doubled the absorbance (Fig. 23). These results suggested that the enhancement occurs in the early stages of reagent addition (possibly during PAM bromination). When the next reagent was added the catalytic reaction of maleic acid was quenched and no further enhancement occurred. Therfore, the time between reagent addition became crucial. The plausibility of this hypothesis was not investigated or tested. It sufficed to say that maleic acid had a negligible influence on the reaction when less than 3 mg.

Over 0.5 mg of humic acid caused colour development in addition to the colour induced by PAM (Fig. 24). The high absorbances were a result of oxidation of iodide and the absorbance of humic acid itself. The effect was found not to be dependent on ionic strength conditions.

Introduction of saturated oil solutions had no effect on the reactions in the method. However, turbidity sometimes caused slightly higher absorbances.

TABLE 2
EFFECT OF INTERFERENCES ON THE LEUCO CRYSTAL VIOLET METHOD

CONTAMINANT	MIN. AMT. FOR AN EFFECT	EFFECT ON COLOUR INTENSITY	NATURE OF INTERFERENCE	FIGURE #
Sodium Sulphate	10 mg	negative	ionic strength	5
Divalent Calcium	0.2 mg	negative	ionic strength	8,9
Divalent Magnesium	1 mg	negative	ionic strength	7
Divalent Zinc	>10 mg	none	--	6
Ferrous Ion	0.5 mg	net null	ferric bromide abs. ionic strength bromine depletion	10
Ferric Ion	0.01 mg	net negative	ferric bromide abs. ionic strength bromine depletion	11,12
Trivalent Aluminium	1 mg	negative	ionic strength	13,14
Sodium	<300 mg	negative	ionic strength	5
Ammonium	1 mg	negative	bromine depletion	16
Chloride	30 mg	negative	unknown	15
Phosphate	>10 mg	none	--	17
Nitrate	0.2 mg	positive	colour development	8,18
Iodide	0.4 mg	positive	colour development	19
Phenol	0.02 mg	positive	colour development	20
Acetone	30 mg	positive	colour enhancement	21
Maleic Acid	3 mg	positive	inconsistent results	22,23
Humic Acid	0.5 mg	positive	colour development	24
Oil	--	none	--	--

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Part III

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PART III

EFFECT OF pH ON COLOUR INTENSITY
Figure 1

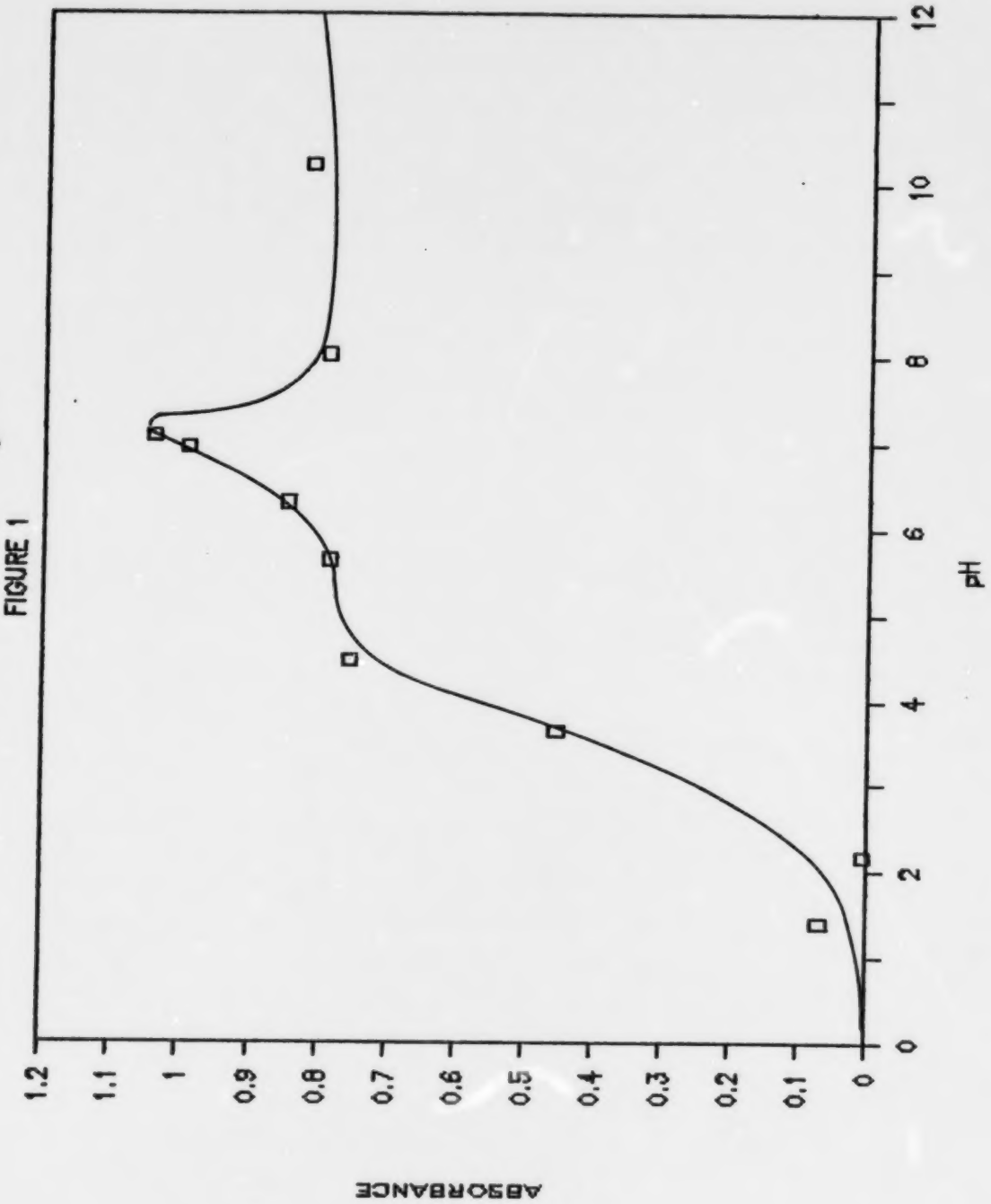
Final Adjusted pH	Absorbance
1.40	0.070
2.18	0.007
3.63	0.454
4.46	0.756
5.63	0.784
6.30	0.847
6.95	0.993
7.08	1.042
8.01	0.788
10.22	0.815

Experimental Conditions:

Experiment #..... LCV 17
Final Volume..... 50 ml
Mass PAM..... 257 ug
Path Length..... 1 cm
Wavelength..... 592 nm

EFFECT OF pH

FIGURE 1



PART III

PAM CURVES; EFFECT OF BUFFER TYPE
Figure 2

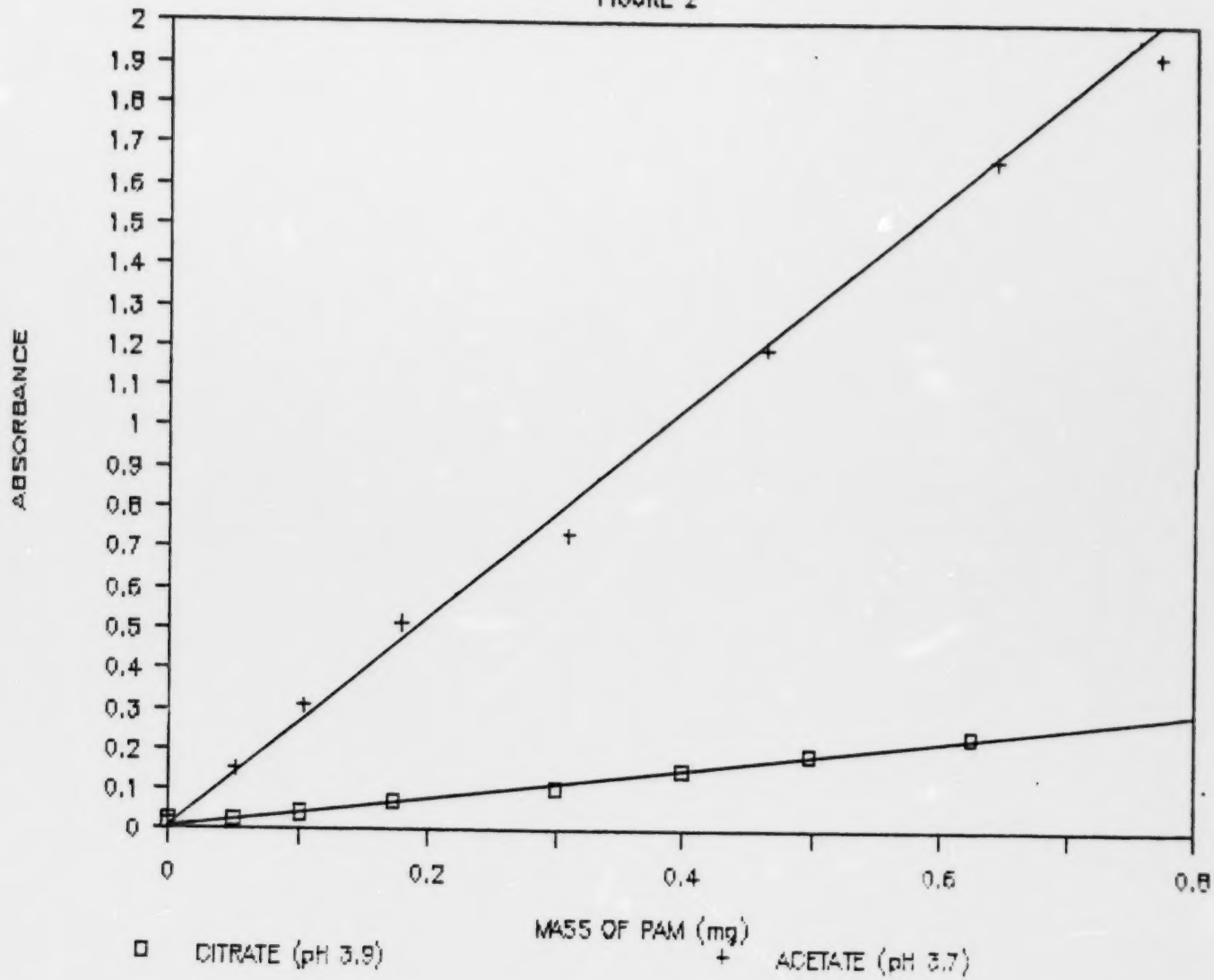
Dry Mass of Polyacrylamide (mg)	Absorbance	
	Citrate Buffer pH = 3.9	Acetate Buffer pH = 3.7
0.000	0.022	0.029
0.050	0.027	1000.000
0.051	1000.000	0.151
0.100	0.042	1000.000
0.103	1000.000	0.308
0.174	0.070	1000.000
0.180	1000.000	0.512
0.299	0.105	1000.000
0.309	1000.000	0.733
0.399	0.148	1000.000
0.464	1000.000	1.195
0.498	0.191	1000.000
0.644	1000.000	1.661
0.624	0.233	1000.000
0.773	1000.000	1.924

Experimental Conditions:		
Experiment #	LCV	LCV
Final Volume	50 ml	50 ml
Dry Mass PAM	148 ug	148 ug
Mass Sodium Sulphate	0.5 g	0 g
Path Length	1 cm	1 cm
Wavelength	592 nm	592 nm

NOTE: When an absorbance value was not obtained for a given mass of polyacrylamide, an arbitrary absorbance value of 1000 was entered in the table.

PAM CURVES; EFFECT OF BUFFER TYPE

FIGURE 2



PART III

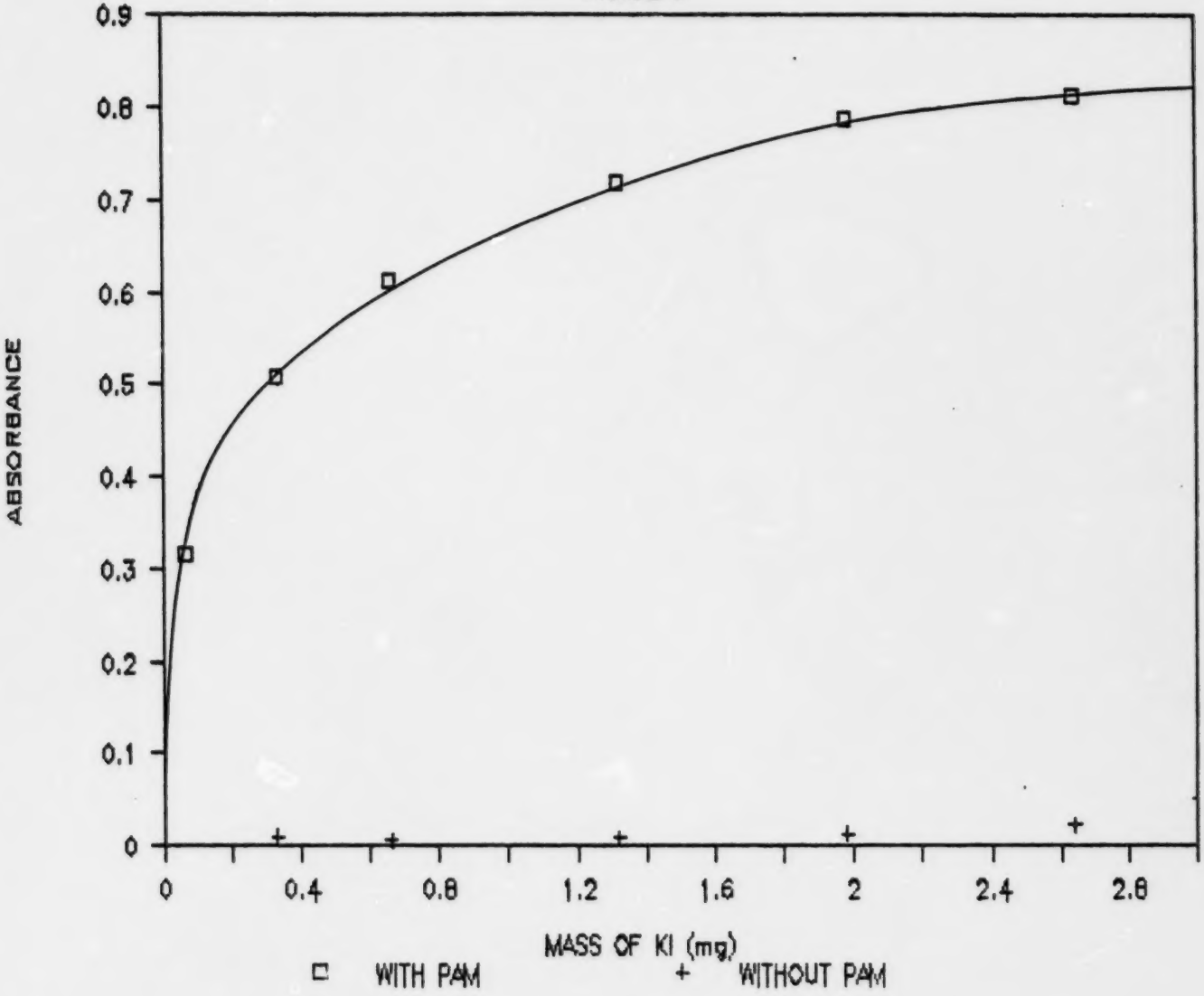
OPTIMISATION OF POTASSIUM IODIDE
Figure 3

Mass of Potassium Iodide (mg)	Absorbance: Constant PAM	Absorbance: Without PAM
0.066	0.315	1000.000
0.330	0.509	0.009
0.660	0.613	0.006
1.320	0.719	0.008
1.980	0.788	0.013
2.640	0.813	0.023
Experimental Conditions:		
Experiment #	LCV 7	LCV 7
Final Volume	50 ml	50 ml
Dry Mass PAM	498 ug	0 ug
Mass Sodium Sulphate	0 g	0 g
Path Length	1 cm	1 cm
Wavelength	592 nm	592 nm

NOTE: When an absorbance value was not obtained for a given given mass of potassium iodide, an arbitrary absorbance value of 1000 was entered in the table.

OPTIMIZATION OF KI

FIGURE 3



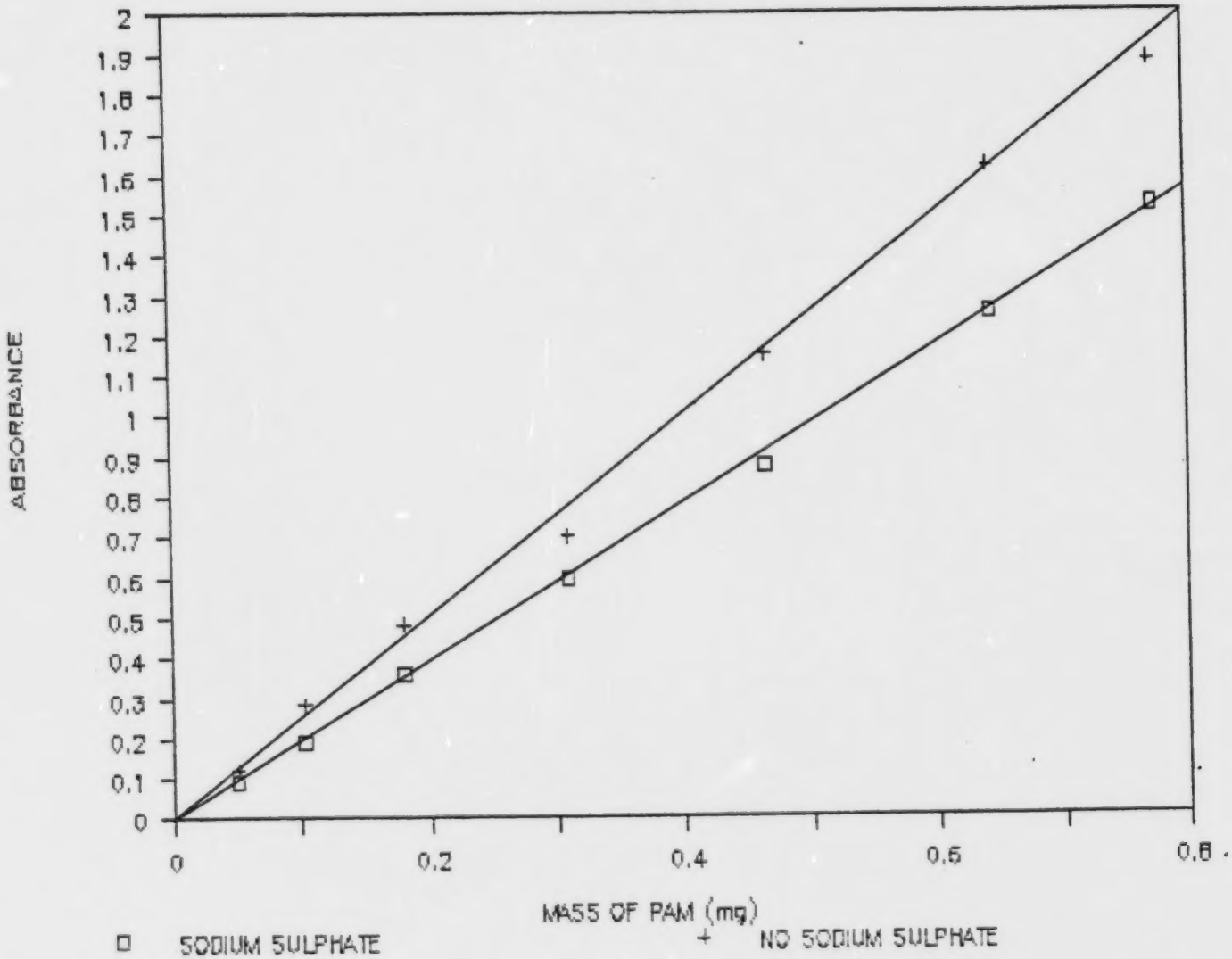
PART III

PAM CONCENTRATION CURVE
Figure 4

#	Dry Mass of Polyacrylamide (ug)	Absorbance - Intercept	
		Constant Ionic Strength	Standard Conditions
1	0.0	0.010	-0.007
2	51.4	0.103	0.111
3	103.0	0.200	0.274
4	180.1	0.369	0.474
5	308.8	0.603	0.693
6	463.3	0.884	1.144
7	643.5	1.265	1.613
8	772.2	1.529	1.874
Linear Statistics:			
Points Used		2-8	2-8
Intercept		0.012	0.046
Correlation Coefficient		1.000	0.999
1/Slope		702.9	588.3
Experimental Conditions:			
Experiment #		LCV 41	LCV 42
Final Volume		50 ml	50 ml
Mass Sodium Sulphate		0.5 g	0 g
Path Length		1 cm	1 cm
Wavelength		592 nm	592 nm

PAM CONCENTRATION CURVE

FIGURE 4



PART III

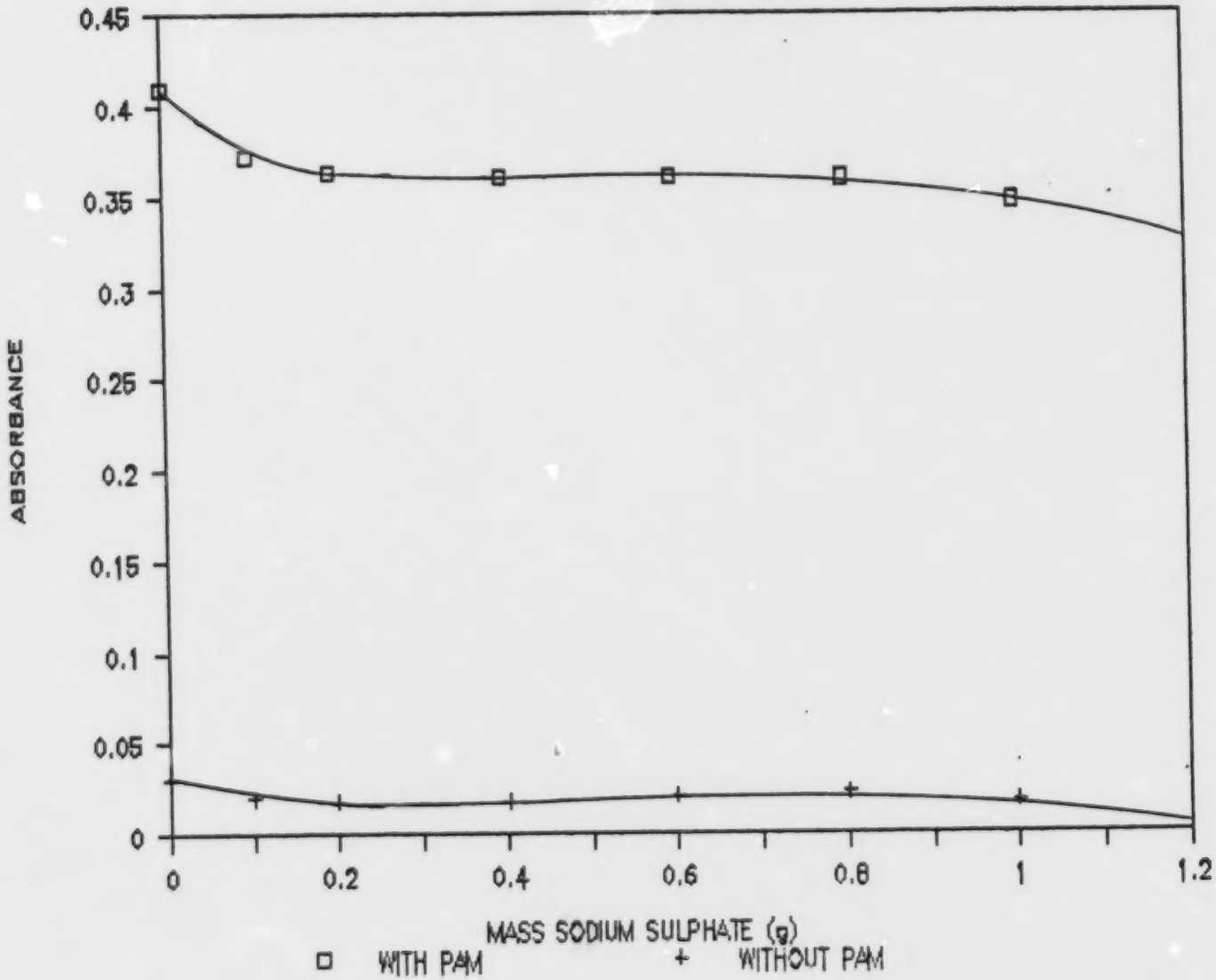
EFFECT OF SODIUM SULPHATE
Figure 5

Mass of Sodium Sulphate (g)	Absorbance: Constant PAM	Absorbance: Without PAM
0.0	0.409	0.030
0.1	0.372	0.020
0.2	0.364	0.018
0.4	0.361	0.018
0.6	0.361	0.021
0.8	0.360	0.023
1.0	0.347	0.018

Experimental Conditions:		
Experiment #	LCV 27	LCV 28
Final Volume	50 ml	50 ml
Dry Mass PAM	129 ug	0 ug
Path Length	1 cm	1 cm
Wavelength	592 nm	592 nm

EFFECT OF SODIUM SULPHATE

FIGURE 5



PART III

EFFECT OF ZINC
Figure 6

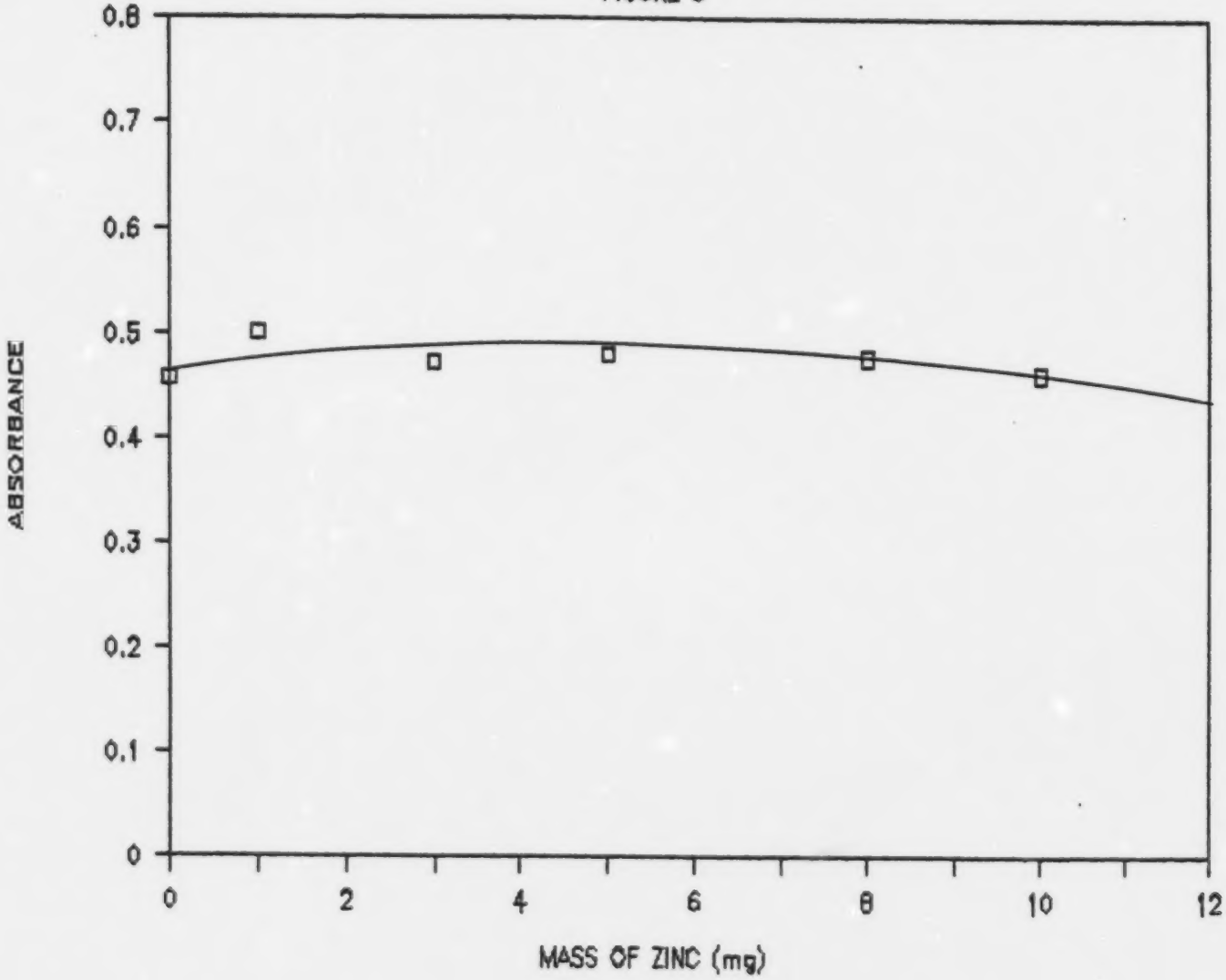
Mass of Zinc (mg)	Absorbance
0	0.458
1	0.501
3	0.473
5	0.480
8	0.476
10	0.461

Experimental Conditions:

Experiment #.....	LCV 37
Final Volume.....	50 ml
Dry Mass PAM.....	205.9
Mass Sodium Sulphate.....	0 g
Path Length.....	1 cm
Wavelength.....	592 nm

EFFECT OF ZINC

FIGURE 6



PART III

EFFECT OF MAGNESIUM
Figure 7

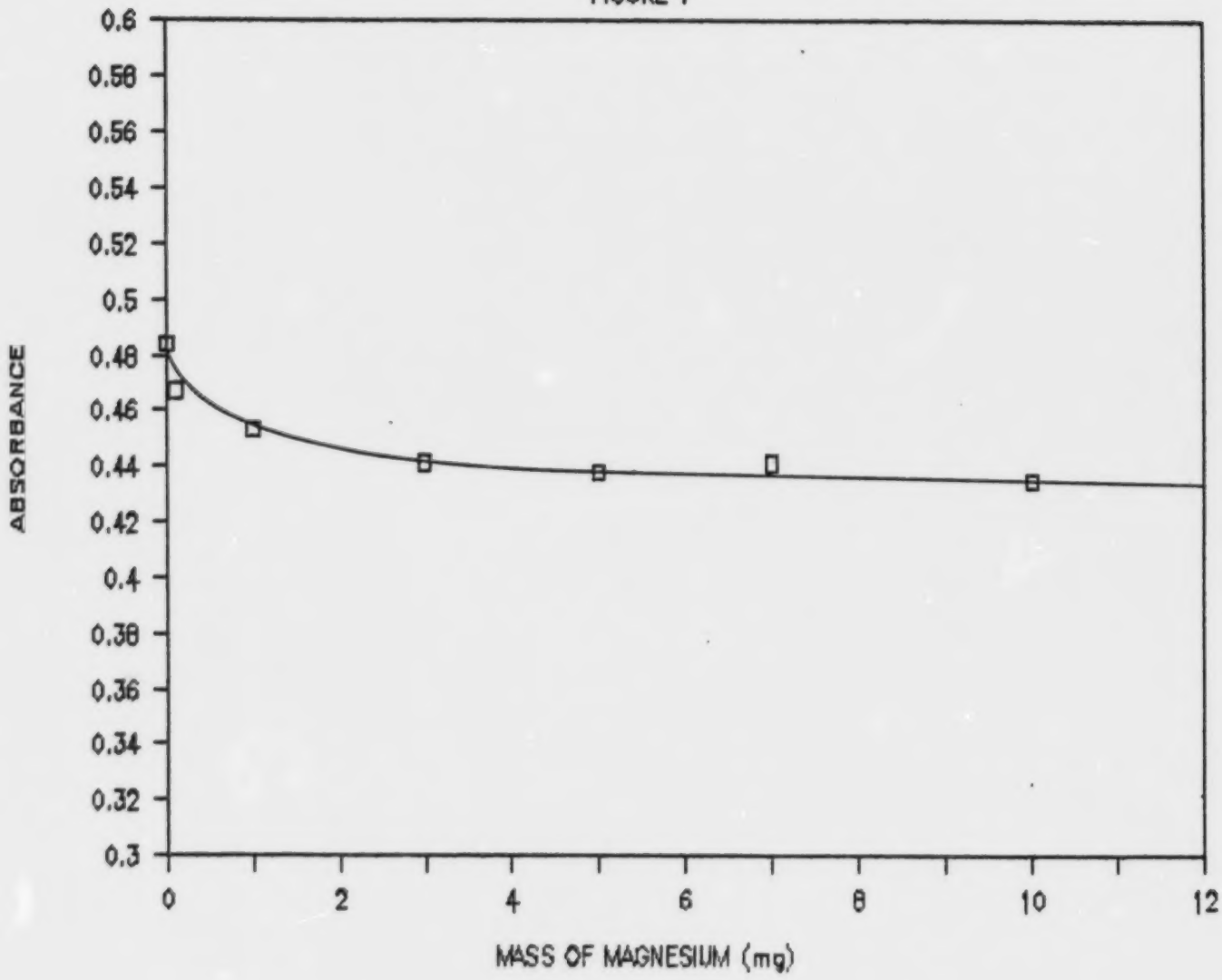
Mass of Magnesium (mg)	Absorbance
0.0	0.484
0.1	0.467
1.0	0.453
3.0	0.441
5.0	0.438
7.0	0.441
10.0	0.435

Experimental Conditions:

Experiment #.....	LCV 45
Final Volume.....	50 ml
Dry Mass PAM.....	206 ug
Mass Sodium Sulphate.....	0 g
Path Length.....	1 cm
Wavelength.....	592 nm

EFFECT OF MAGNESIUM

FIGURE 7



PART III

CALCIUM NITRATE EFFECT;
LOW RANGE
Figure 8

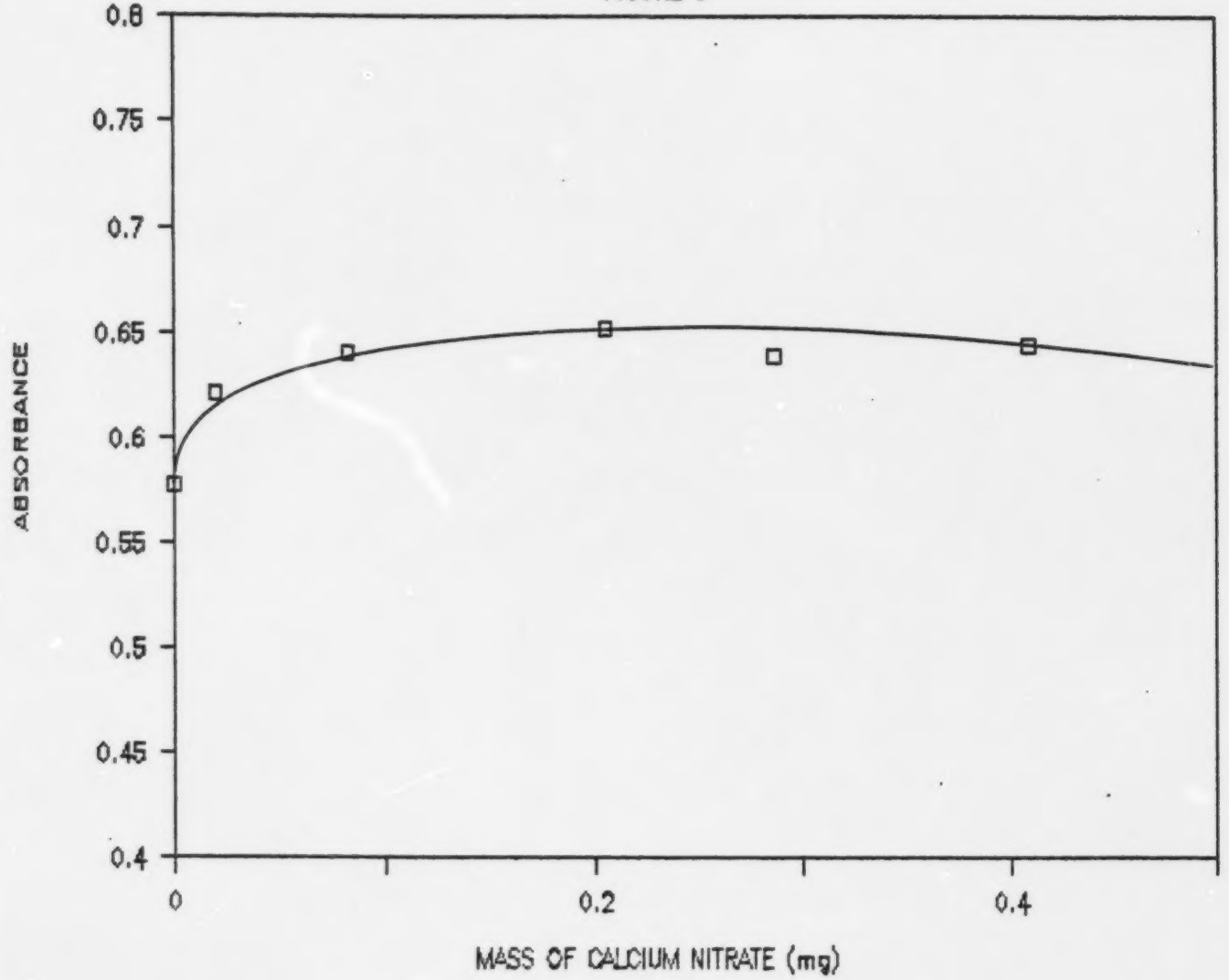
Mass of Calcium Nitrate (mg)	Absorbance
0.000	0.577
0.020	0.621
0.082	0.640
0.205	0.652
0.286	0.639
0.409	0.644

Experimental Conditions:

Experiment #.....	LCV 43
Final Volume.....	50 ml
Dry Mass PAM.....	206 ug
Mass Sodium Sulphate.....	0 g
Path Length.....	1 cm
Wavelength.....	592 nm

CALCIUM NITRATE EFFECT; LOW RANGE

FIGURE 8



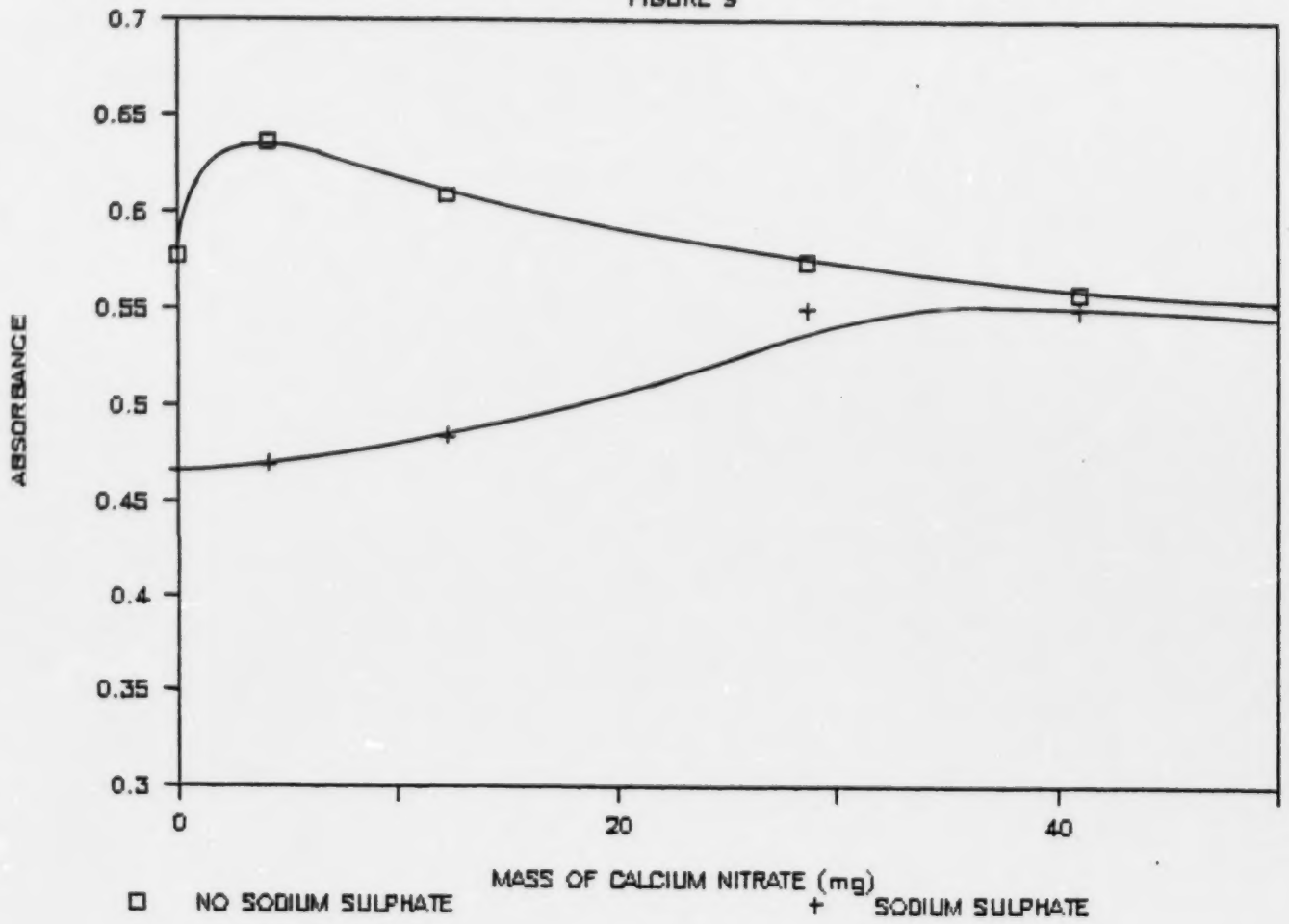
PART III

CALCIUM NITRATE EFFECT;
HIGH RANGE
Figure 9

Mass of Calcium Nitrate (mg)	Absorbance: Constant Ionic Strength	Absorbance: Standard Conditions
0.0	0.465	0.577
4.1	0.469	0.636
12.3	0.484	0.609
28.7	0.549	0.574
41.0	0.549	0.558
Experimental Conditions:		
Experiment #	LCV 44	LCV 43
Final Volume	50 ml	50 ml
Dry Mass PAM	206 ug	206 ug
Mass Sodium Sulphate	0.5 g	0 g
Path Length	1 cm	1 cm
Wavelength	592 nm	592 nm

CALCIUM NITRATE EFFECT; HIGH RANGE

FIGURE 9



PART III

EFFECT OF FERROUS ION
Figure 10

Mass of Ferrous Ion (mg)	Absorbance: Constant Ionic Strength	Absorbance: Standard Conditions *	Absorbance: Without PAM
0.0	0.487	0.420	0.017
0.5	0.515	0.416	1000.000
1.0	0.507	0.416	1000.000
3.0	0.501	0.418	0.025
5.0	0.490	0.403	1000.000
8.0	0.483	0.392	0.053
10.0	0.482	0.382	0.063

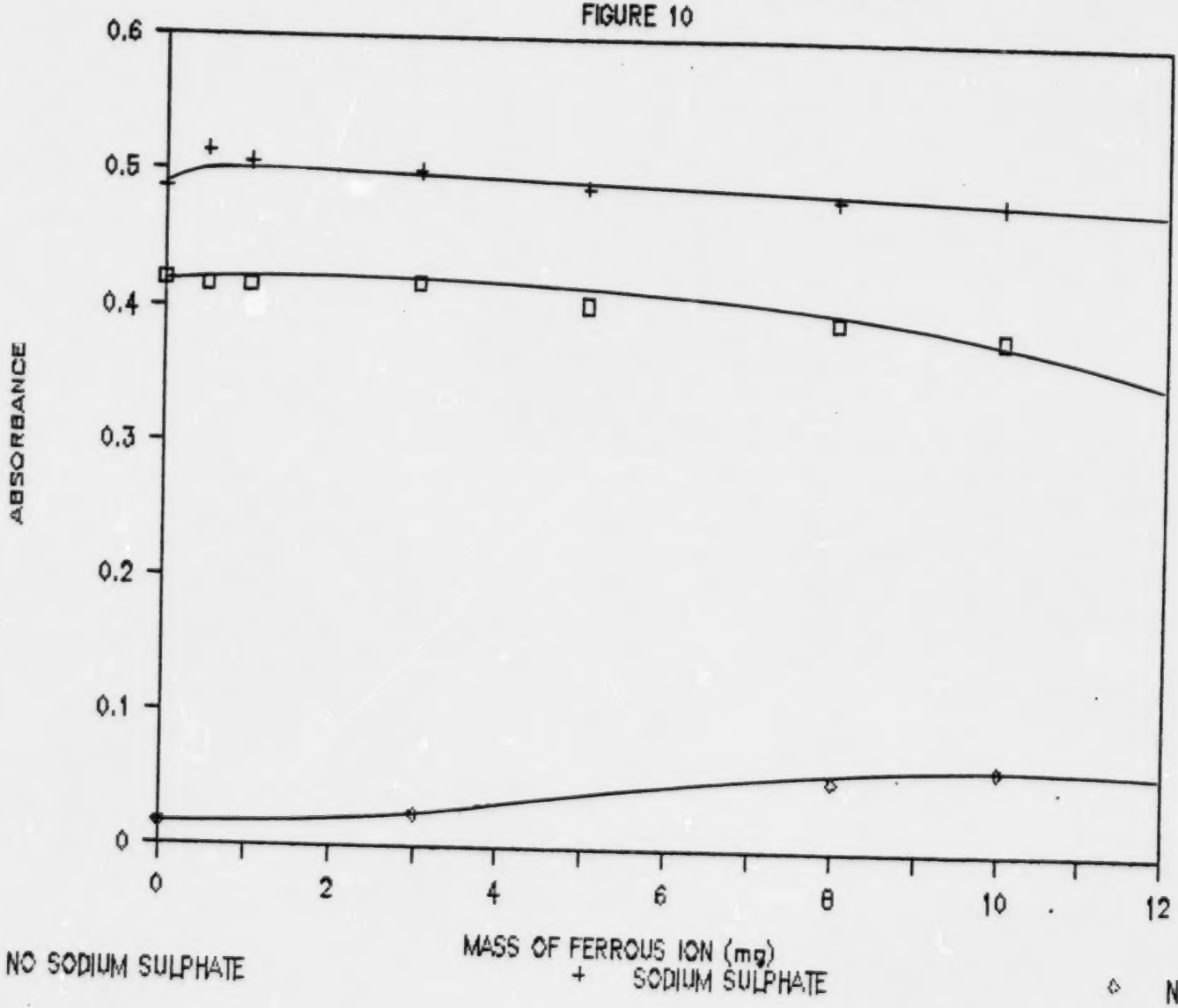
Experimental Conditions:			
Experiment #	LCV 97	LCV 96	LCV 98
Final Volume	50 ml	50 ml	50 ml
Dry Mass PAM	218 ug	218 ug	0 ug
Mass Sodium Sulphate	0.5 g	0 g	0 g
Path Length	1 cm	1 cm	1 cm
Wavelength	592 nm	592 nm	592 nm

NOTE: When an absorbance value was not obtained for a given mass of ferrous ion, an arbitrary absorbance value of 1000 was entered in the table.

* An expired sodium formate reagent solution caused low absorbances.

EFFECT OF FERROUS ION

FIGURE 10



PART III

EFFECT OF Fe3+;
LOW RANGE
Figure 11

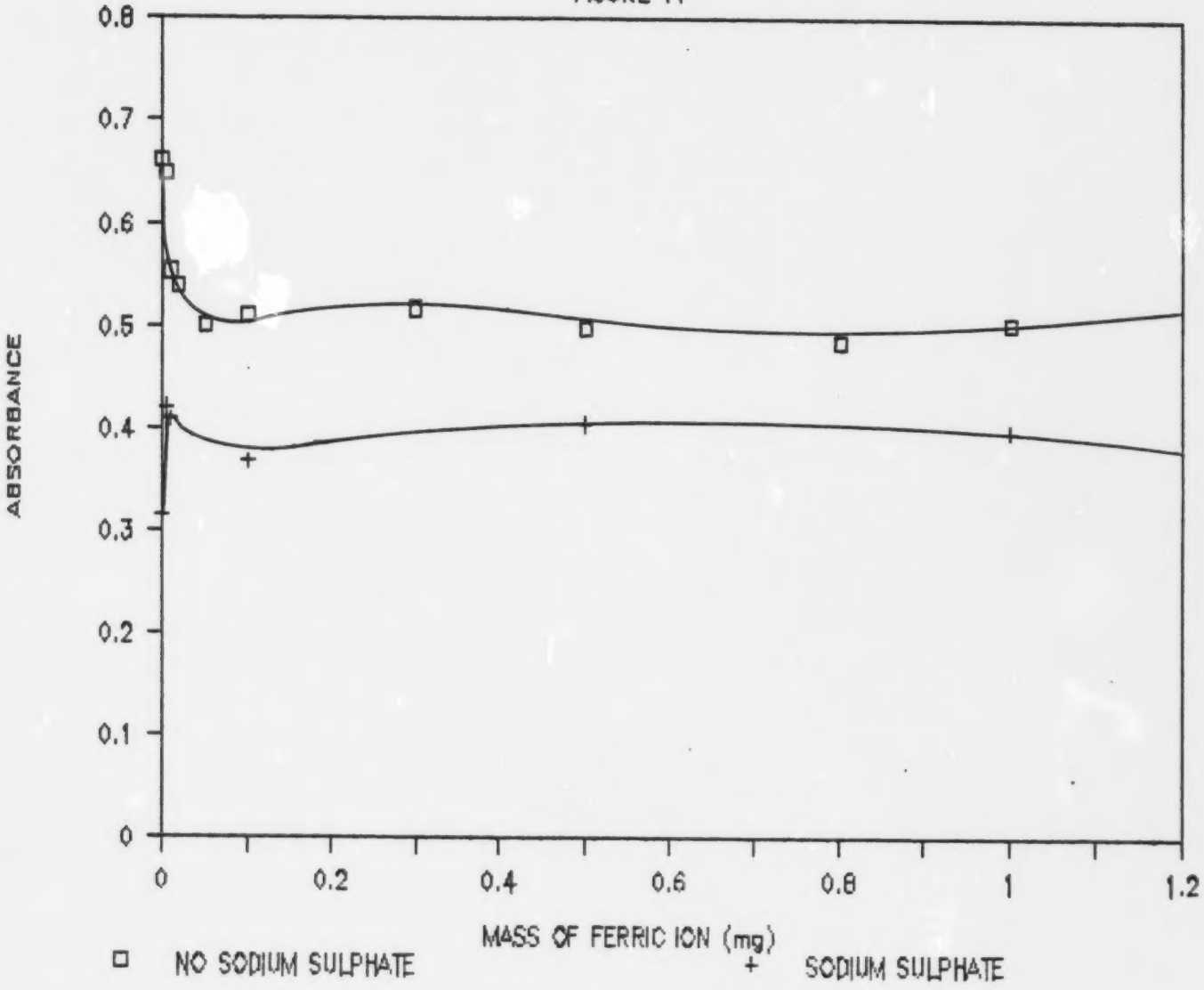
Mass of Ferric Ion (mg)	Absorbance: Constant Ionic Strength	Absorbance: Standard Conditions
0.000	0.316	0.662
0.005	0.420	0.648
0.010	0.409	0.553
0.020	1000.000	0.540
0.050	1000.000	0.500
0.100	0.368	0.510
0.300	1000.000	0.517
0.500	0.405	0.499
0.800	1000.000	0.485
1.000	0.398	0.503

Experimental Conditions:		
Experiment #	LCV 33	LCV 92
Final Volume	50 ml	50 ml
Dry Mass PAM	206 ug	218 ug
Mass Sodium Sulphate	0.5 g	0 g
Path Length	1 cm	1 cm
Wavelength	592 nm	592 nm

NOTE: When an absorbance value was not obtained for a given mass of ferric ion, an arbitrary absorbance value of 1000 was entered in the table.

EFFECT OF Fe3+; LOW RANGE

FIGURE 11



PART III

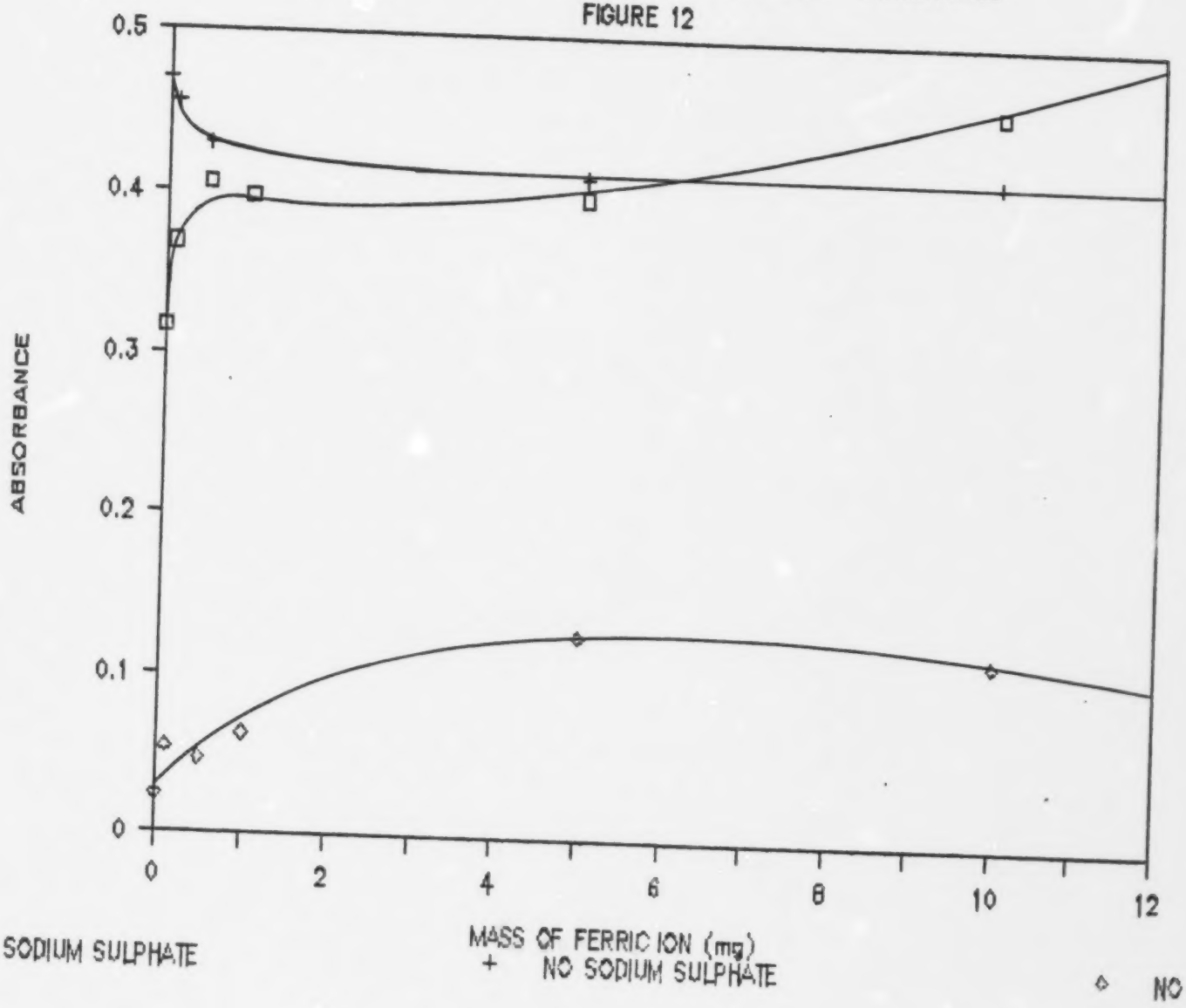
EFFECT OF Fe3+;
HIGH RANGE
Figure 12

Mass of Ferric Ion (mg)	Absorbance: Constant Ionic Strength	Absorbance: Standard Conditions	Absorbance: Without PAM
0.0	0.316	0.470	0.024
0.1	0.368	0.455	0.054
0.5	0.405	0.430	0.047
1.0	0.398	1000.000	0.063
5.0	0.400	0.413	0.127
10.0	0.458	0.415	0.116
Experimental Conditions:			
Experiment #	LCV 33	LCV 34	LCV 36
Final Volume	50 ml	50 ml	50 ml
Dry Mass PAM	206 ug	206 ug	0 ug
Mass Sodium Sulphate	0.5 g	0 g	0 g
Path Length	1 cm	1 cm	1 cm
Wavelength	592 nm	592 nm	592 nm

NOTE: When an absorbance value was not obtained for a given mass of ferric ion, an arbitrary absorbance value of 1000 was entered in the table.

EFFECT OF Fe3+; HIGH RANGE

FIGURE 12



PART III

EFFECT OF ALUMINIUM;
LOW RANGE
Figure 13

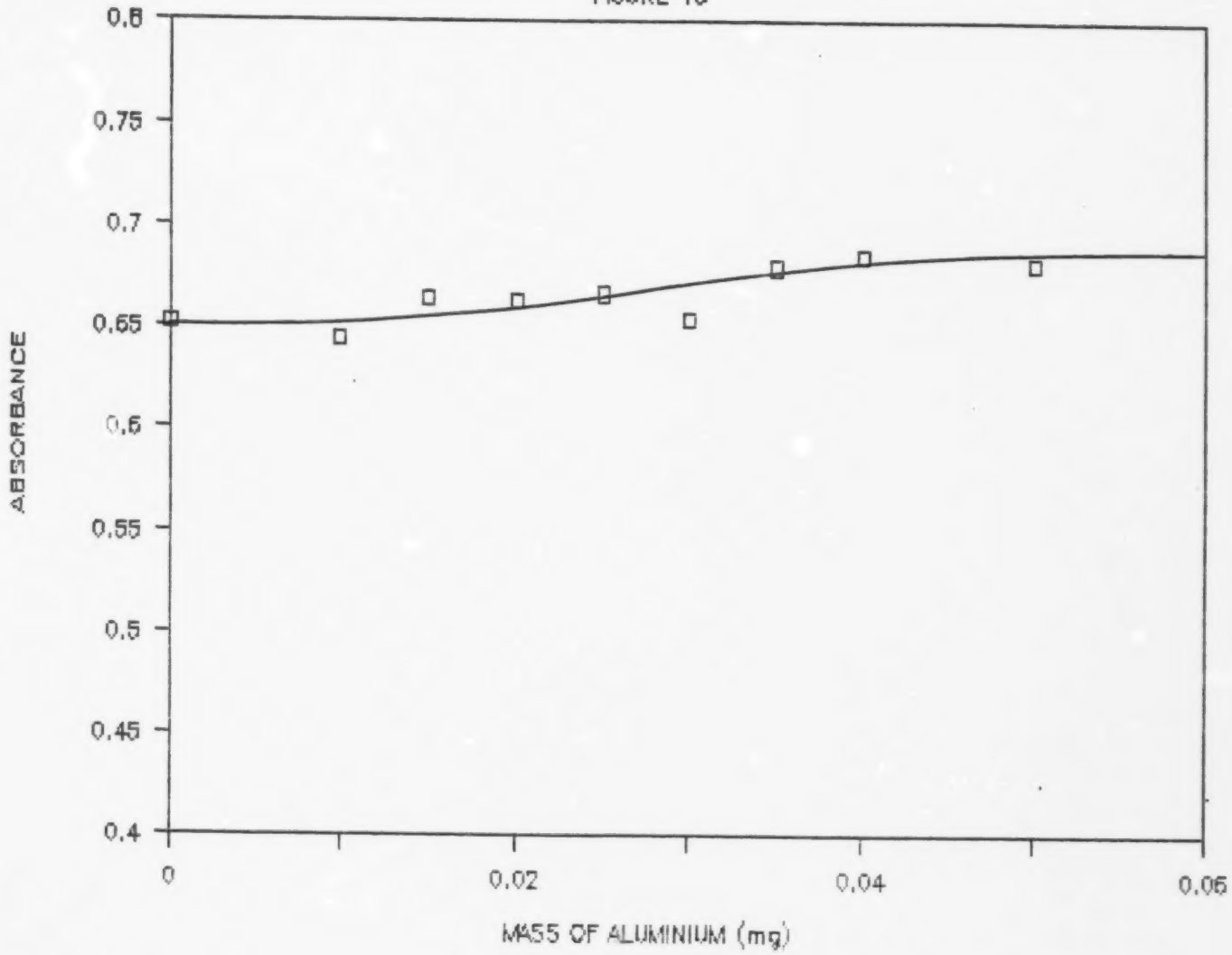
Mass of Aluminium (mg)	Absorbance
0.000	0.652
0.010	0.644
0.015	0.664
0.020	0.663
0.025	0.666
0.030	0.654
0.035	0.679
0.040	0.685
0.050	0.681

Experimental Conditions:

Experiment #.....	LCV 51
Final Volume.....	50 ml
Dry Mass PAM.....	204 ug
Mass Sodium Sulphate.....	0 g
Path Length.....	1 cm
Wavelength.....	592 nm

EFFECT OF Al3+; LOW RANGE

FIGURE 13



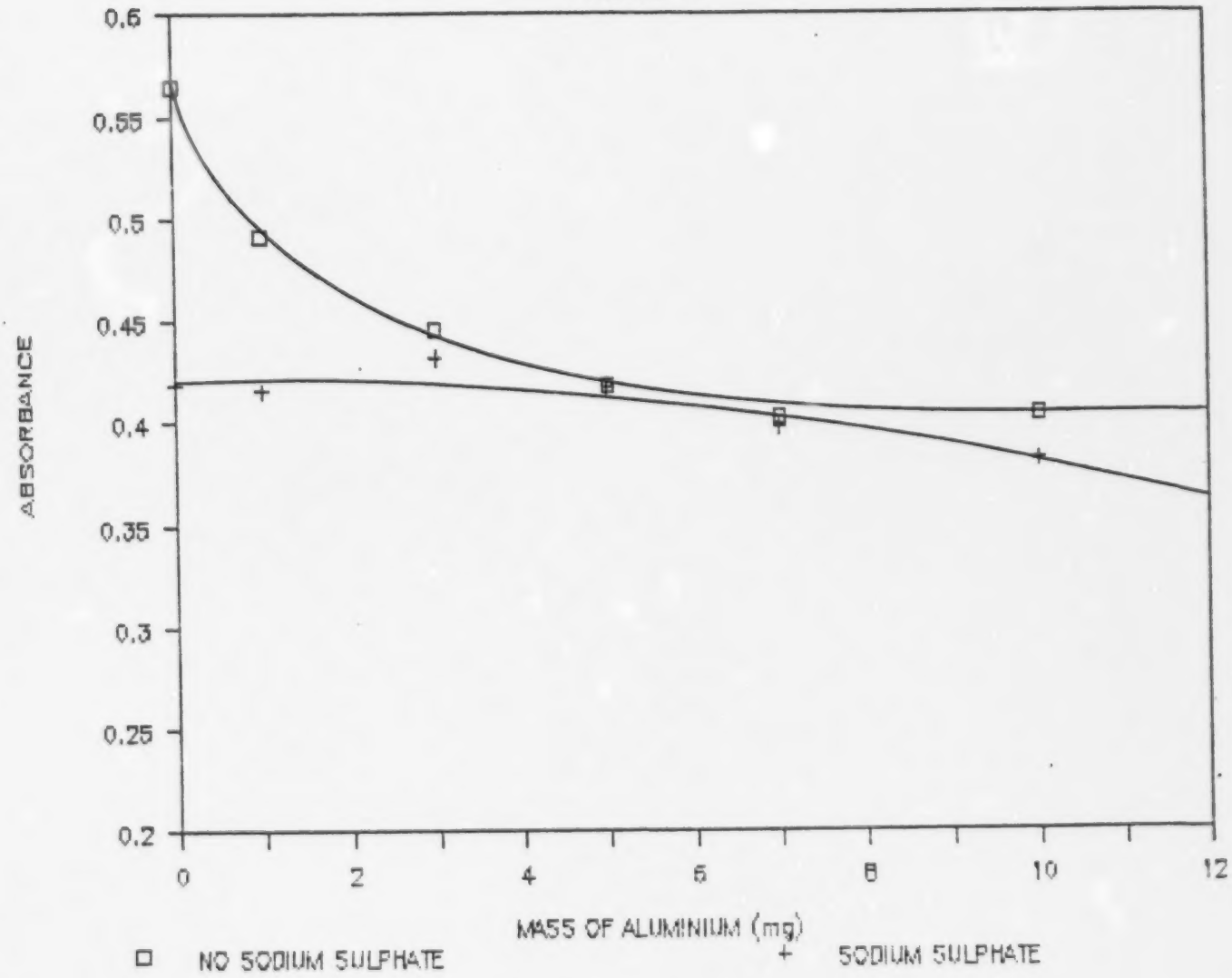
PART III

EFFECT OF Al3+;
HIGH RANGE
Figure 14

Mass of Aluminium (mg)	Absorbance	
	Constant Ionic Strength	Standard Conditions
0	0.419	0.565
1	0.416	0.492
3	0.432	0.446
5	0.417	0.418
7	0.398	0.402
10	0.382	0.404
Experimental Conditions:		
Experiment #	LCV 48	LCV 47
Final Volume	50 ml	50 ml
Dry Mass PAM	206 ug	206 ug
Mass Sodium Sulphate	0.5 g	0 g
Path Length	1 cm	1 cm
Wavelength	592 nm	592 nm

EFFECT OF Al3+; HIGH RANGE

FIGURE 14



PART III

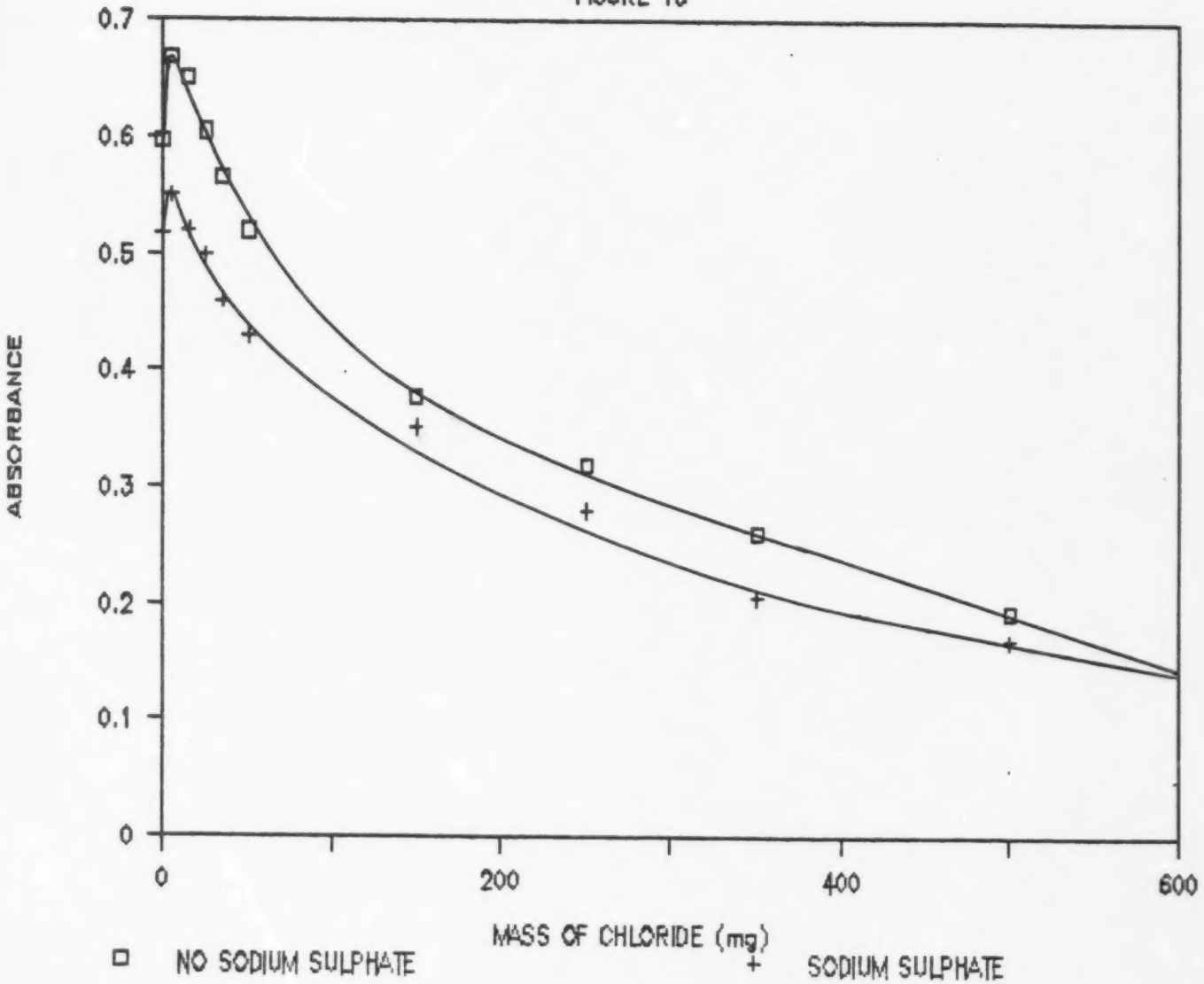
EFFECT OF CHLORIDE;
HIGH RANGE
Figure 15

Mass of Chloride (mg)	Absorbance	
	Constant Ionic Strength	Standard Conditions
0	0.517	0.597
5	0.550	0.669
15	0.520	0.651
25	0.499	0.605
35	0.460	0.565
50	0.430	0.520
150	0.352	0.378
250	0.280	0.319
350	0.206	0.262
500	0.170	0.194

Experimental Conditions:		
Experiment #	LCV 54	LCV 53
Final Volume	50 ml	50 ml
Dry Mass PAM	204 ug	204 ug
Mass Sodium Sulphate	0.5 g	0 g
Path Length	1 cm	1 cm
Wavelength	592 nm	592 nm

EFFECT OF CHLORIDE; HIGH RANGE

FIGURE 15



PART III

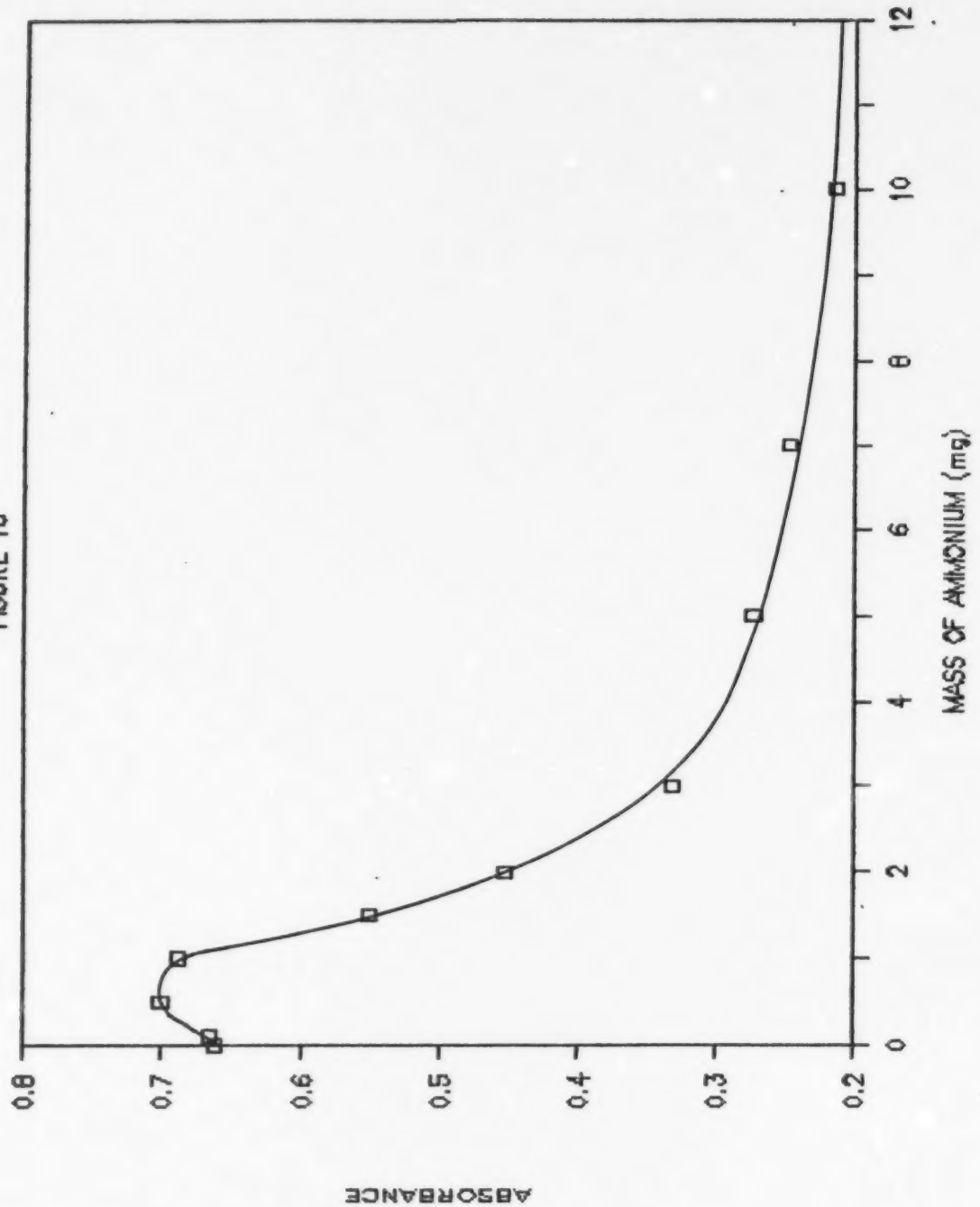
EFFECT OF AMMONIUM
Figure 16

Mass of Ammonium (mg)	Absorbance
0.0	0.662
0.1	0.666
0.5	0.701
1.0	0.689
1.5	0.551
2.0	0.452
3.0	0.332
5.0	0.273
7.0	0.248
10.0	0.215

Experimental Conditions:
- Experiment #.....LCV 59, 88
- Final Volume..... 50 ml
- Dry Mass PAM..... 204 ug
- Mass Sodium Sulphate..... 0 g
- Path Length..... 1 cm
- Wavelength..... 592 nm

EFFECT OF AMMONIUM

FIGURE 16



PART III

EFFECT OF PHOSPHATE
Figure 17

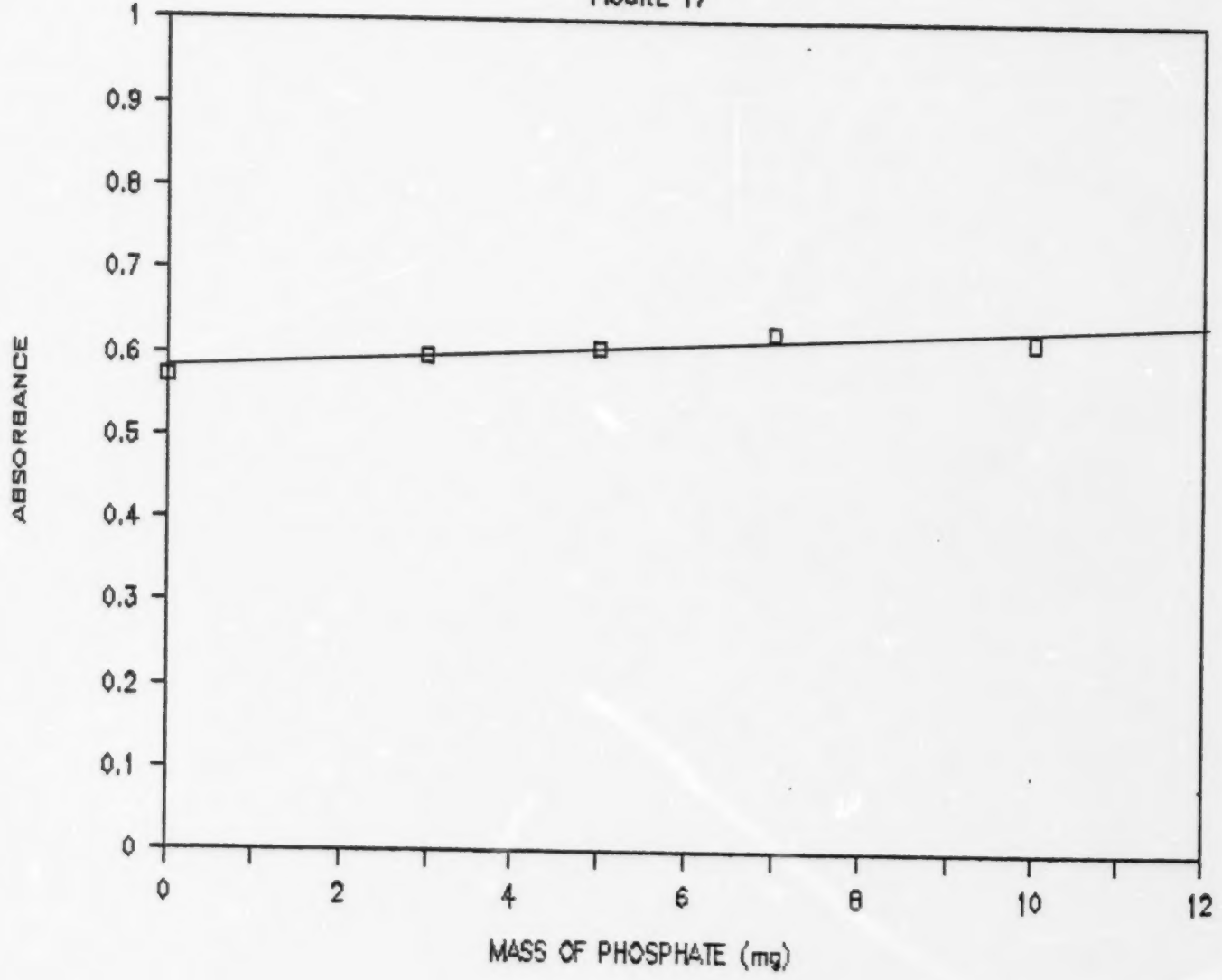
Mass of Phosphate (mg)	Absorbance
0	0.571
3	0.597
5	0.606
7	0.625
10	0.618

Experimental Conditions:

Experiment #.....	LCV 57
Final Volume.....	50 ml
Dry Mass PAM.....	204 ug
Mass Sodium Sulphate.....	0 g
Path Length.....	1 cm
Wavelength.....	592 nm

EFFECT OF PHOSPHATE

FIGURE 17



PART III

EFFECT OF NITRATE
Figure 18

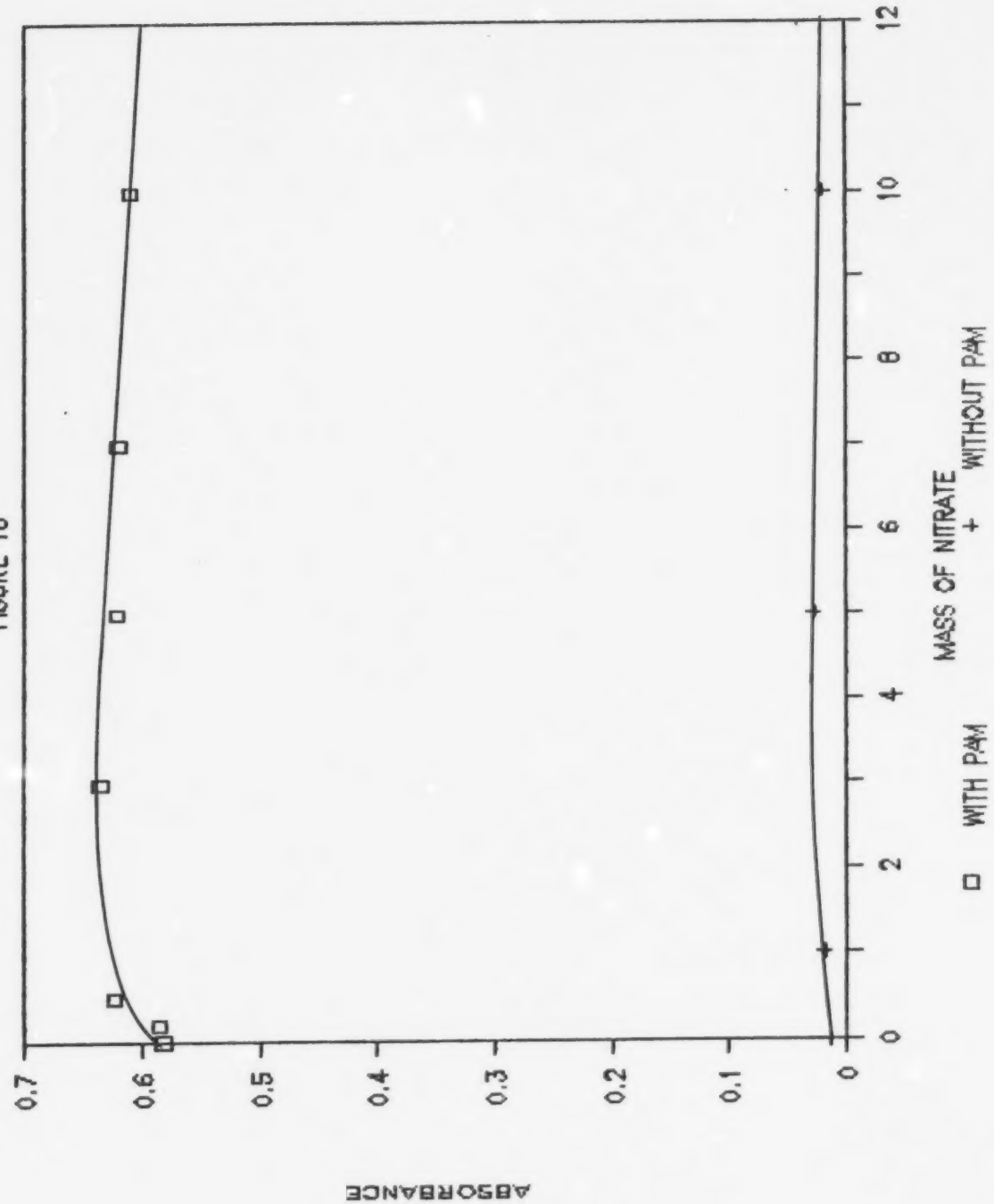
Mass of Nitrate (mg)	Absorbance: Constant PAM	Absorbance: Without PAM
0.0	0.582	0.015
0.2	0.586	1000.000
0.5	0.623	1000.000
1.0	1000.000	0.019
3.0	0.636	1000.000
5.0	0.621	0.028
7.0	0.620	1000.000
10.0	0.610	0.020

Experimental Conditions:		
Experiment #	LCV 102	LCV 103
Final Volume	50 ml	50 ml
Dry Mass PAM	218 ug	0 ug
Mass Sodium Sulphate	0 g	0 g
Path Length	1 cm	1 cm
Wavelength	592 nm	592 nm

NOTE: When an absorbance value was not obtained for a given mass of nitrate, an arbitrary absorbance value of 1000 was entered in the table.

EFFECT OF NITRATE

FIGURE 18



PART III

EFFECT OF IODIDE;
WITHOUT PAM
Figure 19

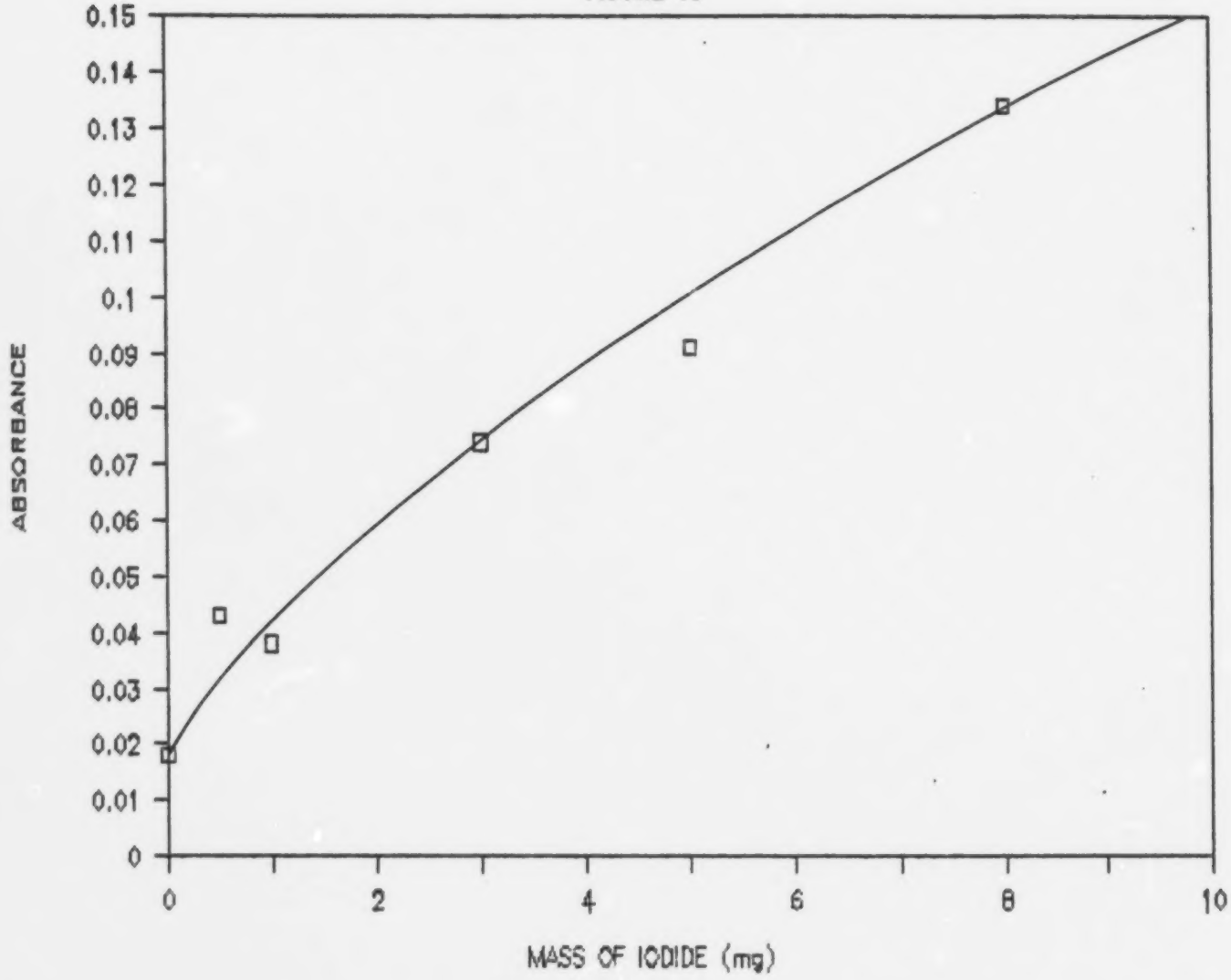
Mass of Iodide (mg)	Absorbance
0.0	0.018
0.5	0.043
1.0	0.038
3.0	0.074
5.0	0.091
8.0	0.134
10.0	1.828

Experimental Conditions:

Experiment #.....	LCV 95
Final Volume.....	50 ml
Dry Mass PAM.....	0 ug
Mass Sodium Sulphate.....	0 g
Path Length.....	1 cm
Wavelength.....	592 nm

EFFECT OF IODIDE; WITHOUT PAM

FIGURE 19



PART III

EFFECT OF PHENOL
Figure 20

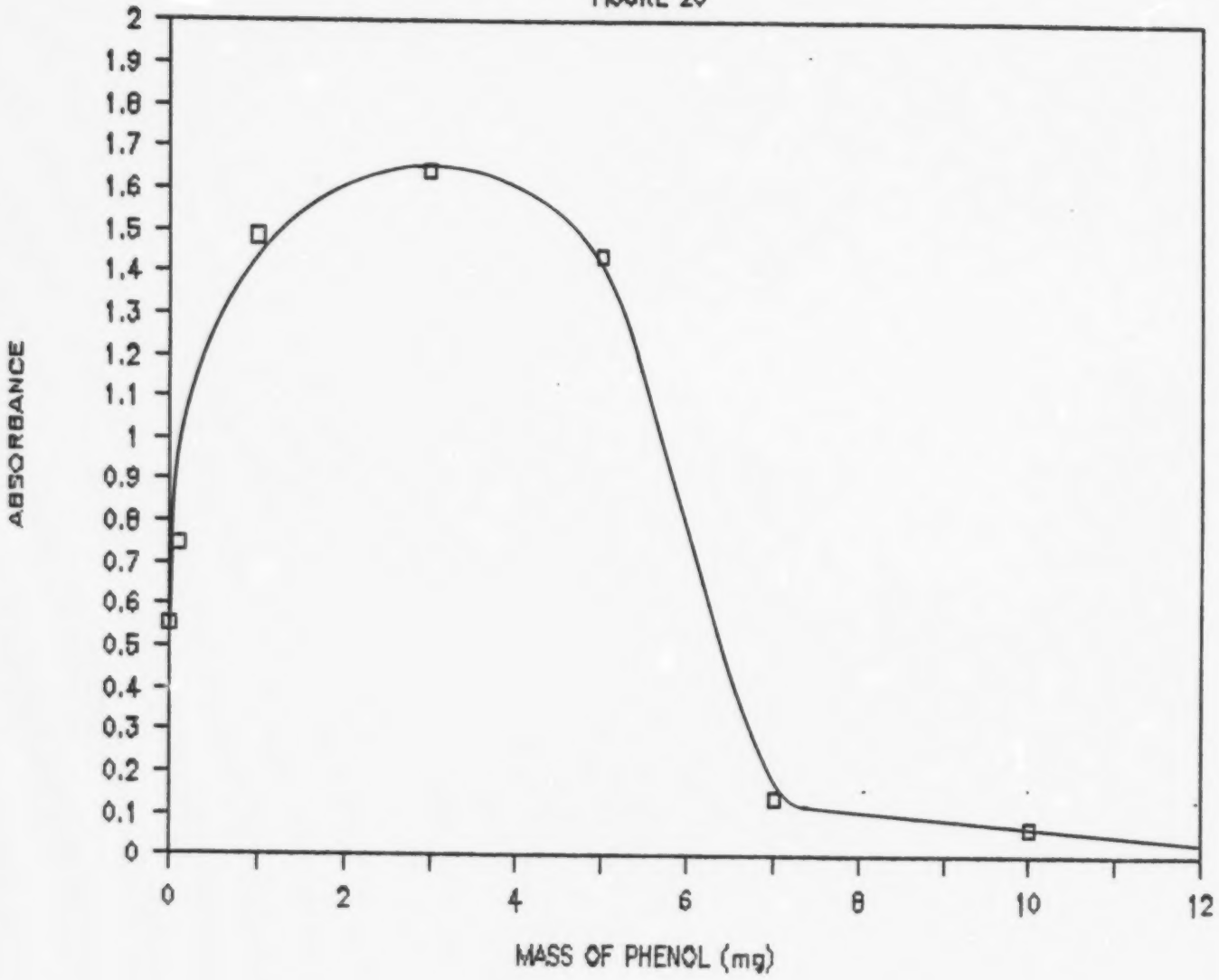
Mass of Phenol (mg)	Absorbance
0.0	0.553
0.1	0.746
1.0	1.485
3.0	1.641
5.0	1.438
7.0	0.138
10.0	0.069

Experimental Conditions:

Experiment #.....	LCV 61
Final Volume.....	50 ml
Dry Mass PAM.....	204 ug
Mass Sodium Sulphate.....	0 g
Path Length.....	1 cm
Wavelength.....	592 nm

EFFECT OF PHENOL

FIGURE 20



PART III

EFFECT OF ACETONE
Figure 21

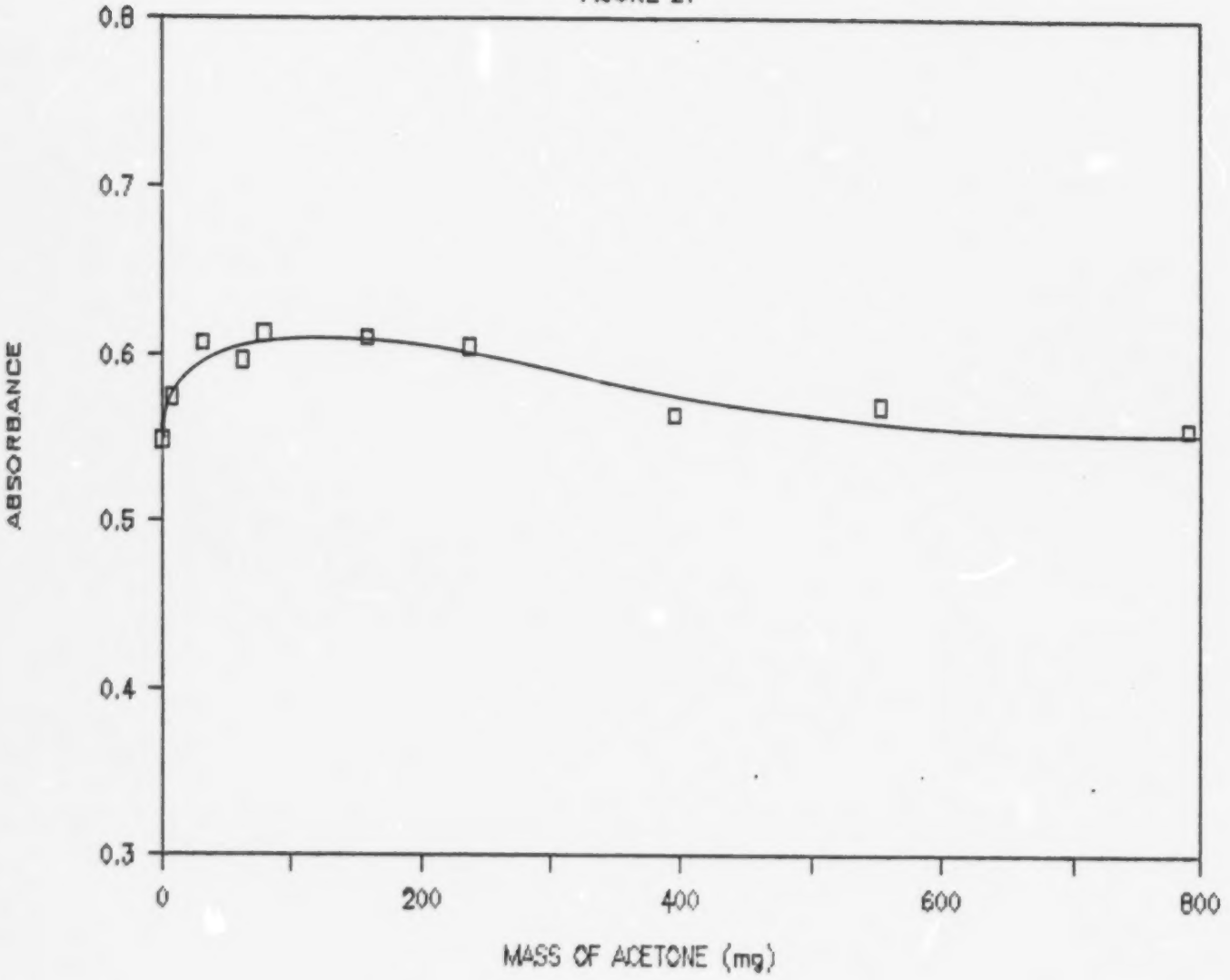
Mass of Acetone (mg)	Absorbance
0.0	0.548
7.9	0.574
31.6	0.606
63.2	0.596
79.0	0.612
158.0	0.610
237.0	0.604
395.0	0.563
553.0	0.569
790.0	0.555

Experimental Conditions:

Experiment #	LCV 63
Final Volume	50 ml
Dry Mass PAM	204 ug
Mass Sodium Sulphate	0 g
Path Length	1 cm
Wavelength	592 nm

EFFECT OF ACETONE

FIGURE 21



PART III

EFFECT OF MALEIC ACID
Figure 22

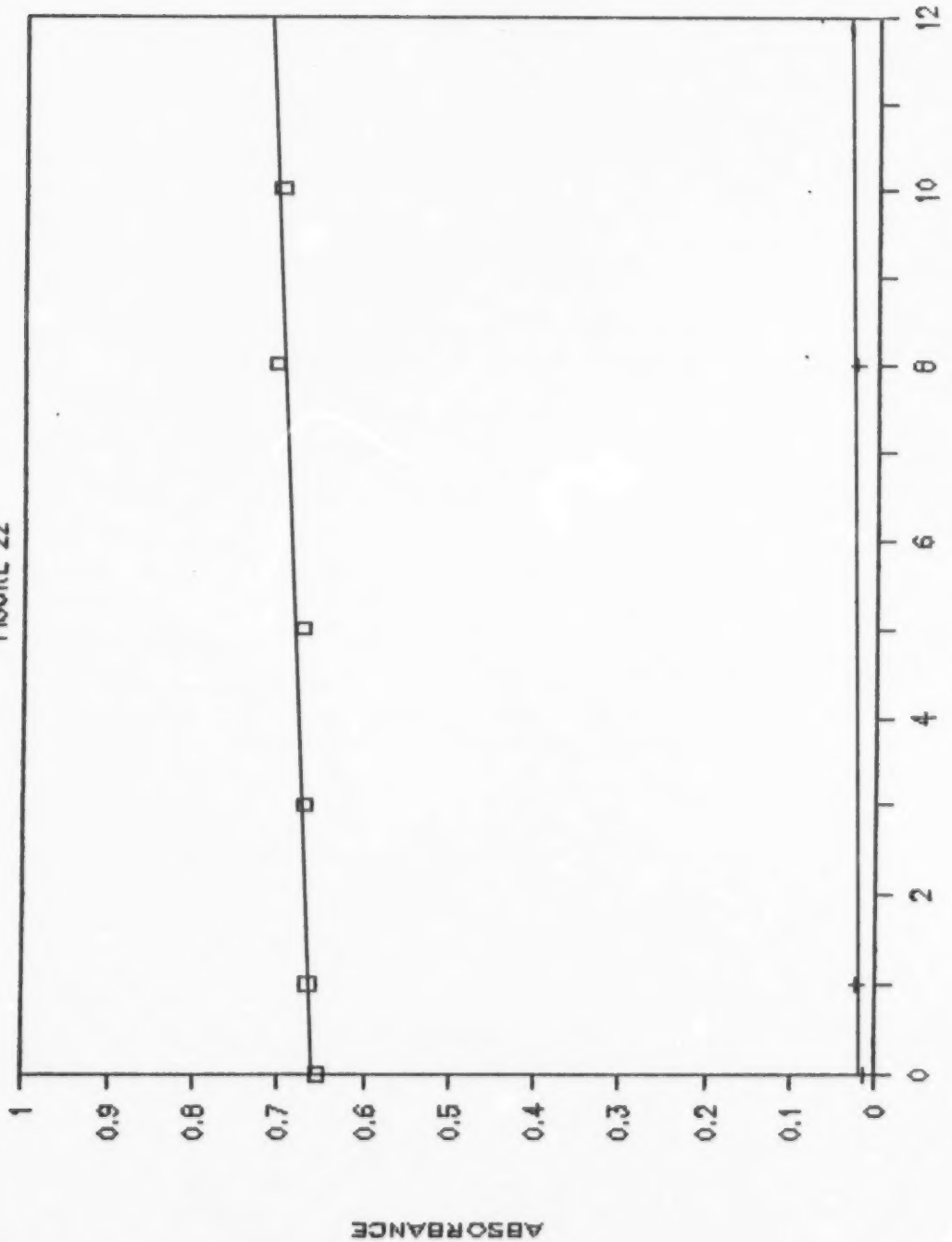
Mass of Maleic Acid (mg)	Absorbance: Constant PAM	Absorbance: Without PAM
0	0.654	0.015
1	0.666	0.022
3	0.670	1000.000
5	0.675	1000.000
8	0.705	0.026
10	0.701	1000.000

Experimental Conditions:		
Experiment #	LCV 104	LCV 105
Final Volume	50 ml	50 ml
Dry Mass PAM	218 ug	0 ug
Mass Sodium Sulphate	0 g	0 g
Path Length	1 cm	1 cm
Wavelength	592 nm	592 nm

NOTE: When an absorbance value was not obtained for a given mass of maleic acid, an arbitrary absorbance value of 1000 was entered in the table.

EFFECT OF MALEIC ACID

FIGURE 22



PART II

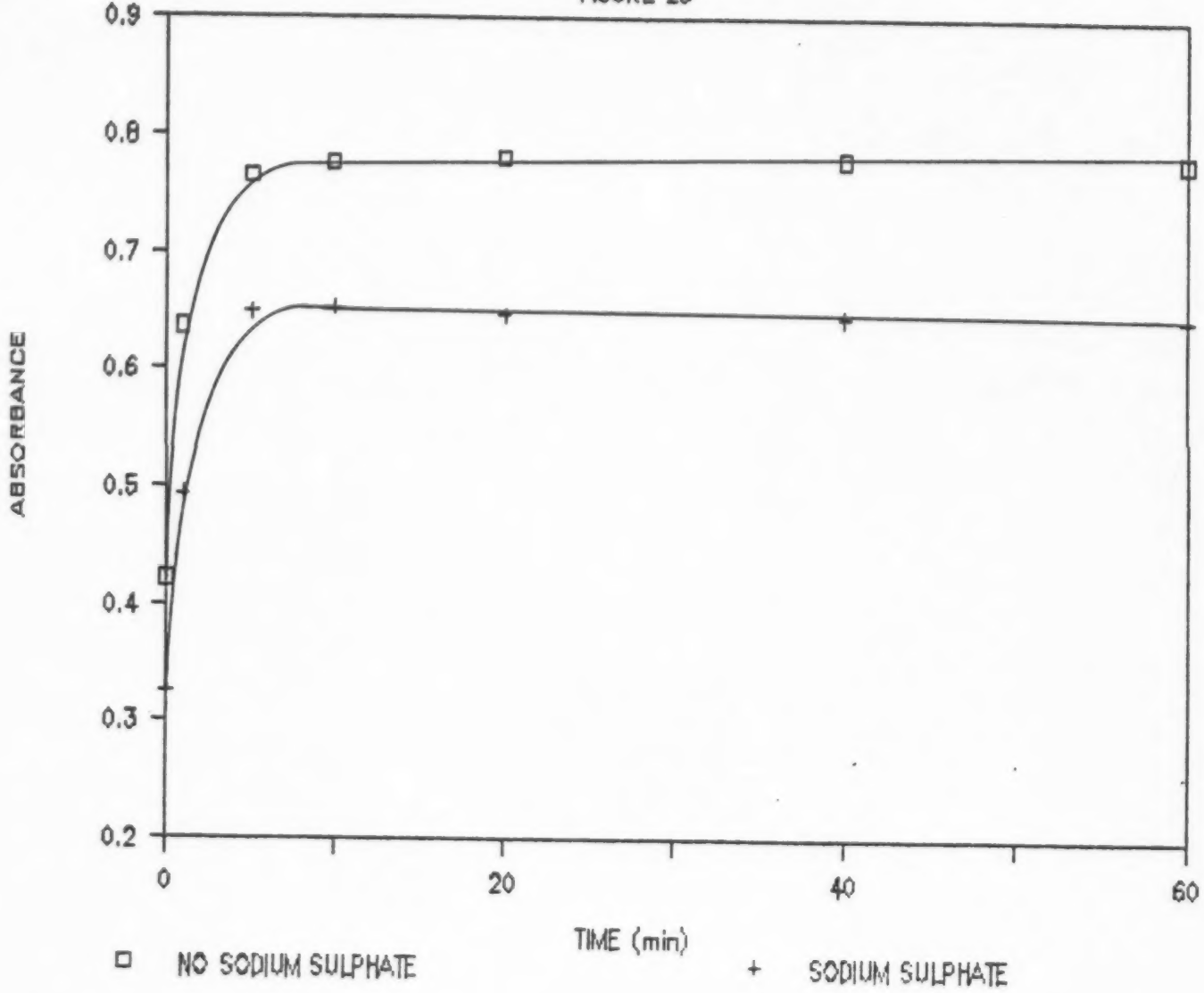
EFFECT OF MALEIC ACID OVER TIME
Figure 23

Time of Reaction (min)	Absorbance: Constant Ionic Strength	Absorbance: Standard Conditions
0	0.325	0.422
1	0.494	0.637
5	0.650	0.766
10	0.653	0.777
20	0.647	0.781
40	0.646	0.780
60	0.645	0.780
120	0.642	0.774

Experimental Conditions:		
Experiment #	LCV 100	LCV 99
Final Volume	50 ml	50 ml
Dry Mass PAM	218 ug	218 ug
Mass Sodium Sulphate	0.5 g	0 g
Path Length	1 cm	1 cm
Wavelength	592 nm	592 nm

EFFECT OF MALEIC ACID OVER TIME

FIGURE 23



PART III

EFFECT OF HUMIC ACID
Figure 24

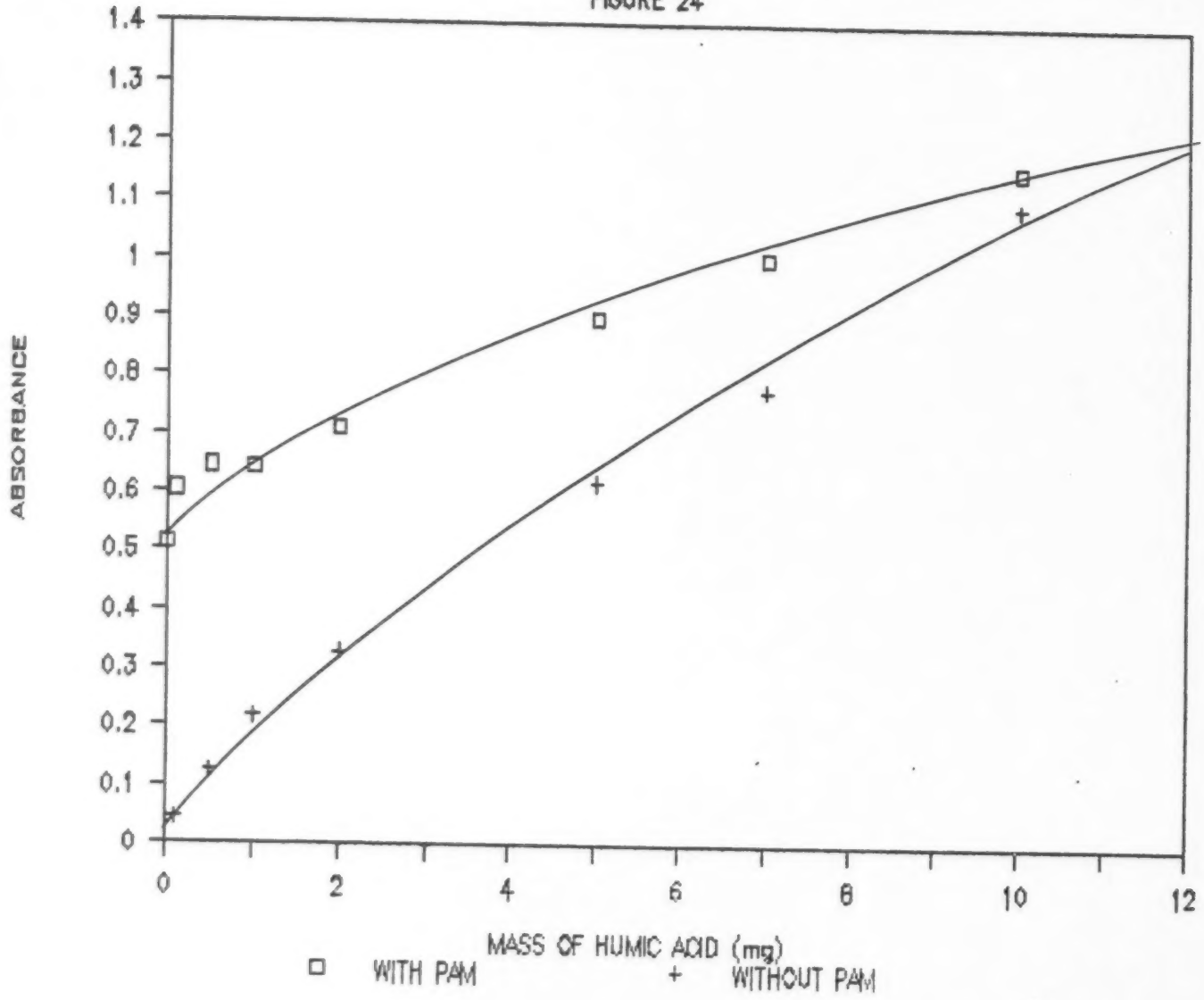
Mass of Humic Acid (mg)	Absorbance: Constant PAM	Absorbance: Without PAM
0.0	0.513	1000.000
0.1	0.605	0.044
0.5	0.646	0.125
1.0	0.644	0.219
2.0	0.711	0.329
5.0	0.898	0.619
7.0	1.000	0.777
10.0	1.155	1.091

Experimental Conditions:		
Experiment #	LCV 71	LCV 72
Final Volume	50 ml	50 ml
Dry Mass PAM	204 ug	0 ug
Mass Sodium Sulphate	0 g	0 g
Path Length	1 cm	1 cm
Wavelength	592 nm	592 nm

NOTE: When an absorbance value was not obtained for a given mass of humic acid, an arbitrary absorbance value of 1000 was entered in the table.

EFFECT OF HUMIC ACID

FIGURE 24



PART IV

Application and Comparison of Various Methods

INTRODUCTION

A comparison of the triiodide, starch-triiodide and leuco crystal violet methods for determination of polyacrylamide in water was made. The comparisons were based on method sensitivity, linearity, and effect of contaminant interferences on the method results. Recoveries of polyacrylamide after filtration and methylene chloride extraction of spiked coal wash waters were also studied. Conclusions were drawn from data obtained in new experimentation as well as information from previous investigations. The methods were compared in terms of application to coal wash water samples.

EXPERIMENTAL

Comparisons of the triiodide, starch-triiodide and leuco crystal violet methods for the determination of polyacrylamide in water was accomplished by applying the procedures described in Parts I, II and III of this series respectively. Reagent preparations and the equipment used were also identical. Experiments performed under constant ionic strength used 5 ml of a 100 g/l sodium sulphate ionic strength buffer solution in the method. Sensitivities for the three methods using various types of polyacrylamides, were compared using standard curves prepared from the same stock polyacrylamide solutions for each type of polyacrylamide studied. Coal wash water samples were introduced to the methods both as contaminants and as samples that were spiked with polyacrylamide. Observations were made regarding the influence of the coal wash water samples on method results and the recovery of polyacrylamide from spiked coal water.

The coal wash water samples were prepared for examination by removing suspended matter and organics. Suspended matter was removed by two gravity filtrations through Whatman number 4 filter paper followed by two more filtrations through number 3 filter paper. Organics were removed from the filtered water by a 3 to 1 aqueous to methlylene chloride extraction. The extracted coal water was boiled for 5 minutes to ensure the complete explusion of methylene chloride. Samples

prepared for the recovery studies were spiked with a known amount of PAM and treated in a similar manner.

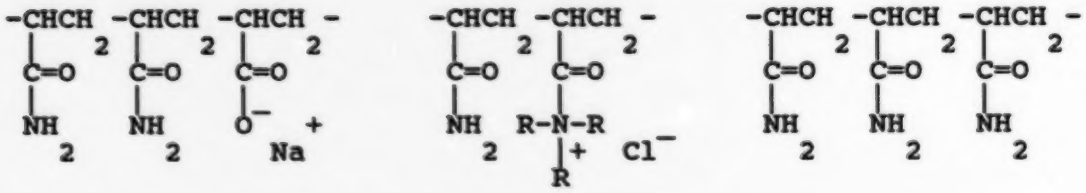
The sensitivity of the leuco crystal violet method was also studied after extraction of the developed colour with methylene chloride. A known volume of methylene chloride extracted the colour developed by polyacrylamide in a known volume of prepared aqueous solution. The methylene chloride layer was dried with sodium sulphate and the absorbance was measured against a methylene chloride reference in one cm cells at a wavelength of 592 nm. Conclusions were drawn from the resulting standard curves for the optimum aqueous to organic volume ratio and the maximum amount of colour (measured in terms of PAM mass required to develop the colour) that a given volume of methylene chloride could extract.

The methods used for the analysis of contaminants in the sample coal waters are described by Franson (1). Elemental analyses of the polyacrylamide standards were performed on a Perkin-Elmer Model 240 Elemental Analyser and a Varian Techtron Atomic Absorption Spectrophotometer. The method for determination of the acrylamide groups on the polyacrylamide standards is described in Appendix 1 at the end of this series.

DISCUSSION AND RESULTS

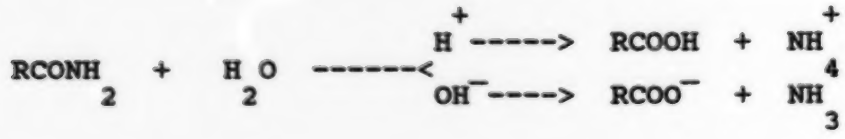
Method Sensitivities

The number of amide groups on a particular type or brand of polyacrylamide is a direct reflection on the extent to which the polymer can be detected by any of the triiodide, starch-triiodide or leuco crystal violet methods. Since the sensitivities of all three methods are dependent on the bromination of the amide group, it follows that colour development is proportional to the number of amide groups available for bromination. Typical structures of various polyacrylamides are shown below:



ANIONIC PAM | CATIONIC PAM | NON-IONIC PAM

Anionic polyacrylamide is formed from the partial hydrolysis of non-ionic PAM. The reaction can proceed under acidic or basic conditions as illustrated below (8):



Elevated temperatures (approximately 200 °C) and a large excess of acid or base are required to undergo complete

hydrolysis. Therefore, the degree of hydrolysis can be controlled through the conditions present during the reaction.

The polyacrylamides examined were anionic, Separan MG 700 (Dow Chemical Co.); catonic, Hercofloc Type 815 (Hercules Incorporated); and nonionic, Hercofloc Type 1027 (Hercules Incorporated). Results of elemental and acrylamide group analysis on the polymers, summarized in Table 1, supported their theoretical structures. Ash (Table 1) and moisture analysis (Table 2) were also performed on the polymers. High oxygen and low amide group content in the anionic polymer analysis results was a direct reflection on the anionic polymer structure. Low oxygen and high acrylamide content was characteristic for the non-ionic polymer, however, it was still partially hydrolysed. It was more difficult to correlate analytical results to theoretical structure for the cationic polymer due to the unknown nature of the organic substituent groups.

Polyacrylamide concentration curves for the anionic (Fig. 1), cationic (Fig. 2) and non-ionic polymers (Fig. 3) were developed to compare the sensitivities between the polymers and between the three methods used. The same comparisons were applied under constant ionic strength conditions (Fig's 4, 5 and 6). A summary of the results (Table 3) confirmed the theoretical proportional relationship between improved sensitivity and number of amide groups for the anionic and

TABLE 1
POLYACRYLAMIDE ANALYSIS RESULTS

PARAMETER	RESULTS OF ANALYSIS (% of dry mass)		
	Dow Separan MG 700 (anionic)	Hercules Hercofloc 815 (cationic)	Hercules Hercofloc 1027 (non-ionic)
Carbon	41.07	46.21	49.46
Hydrogen	5.37	7.58	7.02
Nitrogen	11.04	14.32	18.39
Oxygen	29.89	30.69	20.38
Sodium	12.18	---	0.53
Elemental Recovery	99.55	98.80	95.78
Ash	24.6	0.27	0.73
Acrylamide Groups	49.0	68.6	81.6

TABLE 2
MOISTURE CONTENT IN POLYACRYLAMIDES

POLYACRYLAMIDE	MOISTURE CONTENT (% of total mass)
Dow Separan MG 700 (anionic)	13.1
Hercules Hercofloc 815 (cationic)	11.2
Hercules Hercofloc 1027 (non-ionic)	9.6

TABLE 3
COMPARISON OF METHOD SENSITIVITIES
FOR VARIOUS POLYACRYLAMIDES

METHOD	METHOD SENSITIVITY (ug of PAM *) Value in brackets is correlation coefficient.		
	Anionic, 49.0 % acrylamide groups	Cationic, 68.6 % acrylamide groups	Non-ionic, 81.6 % acrylamide groups
Triiodide	0.3 (0.999)	0.5 (0.999)	0.1 (0.999)
Triiodide; Constant Ionic Strength	0.3 (0.998)	0.5 (1.000)	0.2 (0.999)
Starch-Triiodide	0.2 (1.000)	0.4 (0.999)	0.1 (1.000)
Starch-Triiodide; Constant Ionic Strength	0.3 (0.999)	0.4 (1.000)	0.1 (1.000)
Leuco Crystal Violet	0.4 (0.999)	0.7 (1.000)	0.2 (1.000)
Leuco Crystal Violet; Constant Ionic Strength	0.4 (0.999)	0.5 (0.999)	0.2 (1.000)

* ug of PAM ,in the final volume, required to produce an absorbance of 0.001 units in 1 cm cells.

non-ionic polymers. Also, constant ionic strength tended to slightly inhibit method sensitivities for the anionic and non-ionic polyacrylamides*. However, the cationic polymer seemed to deviate from the original theory. Although the cationic PAM had a larger number of acrylamide groups than the anionic polymer, its sensitivity was impeded due to the steric hinderence from the organic substituents on the cationic nitrogen. Also, constant ionic strength seemed to enhance the sensitivity rather than hinder it for the cationic polymer. These results were similar to those from Scoggins' study on various polyacrylamides applied to the starch-triiodide method.

The triiodide, starch-triiodide and leuco crystal violet methods all had comparable linearities and sensitivities. The correlation coefficients (r^2) revealed that all three methods were linear up to 400 ug of anionic and cationic PAM (Fig's 1 and 2), and 200 ug of non-ionic PAM (Fig. 3). Results were slightly more erratic for cationic PAM analysed by the triiodide method under constant ionic strength conditions so the average values from two curves where used (Fig. 5). Anionic and non-ionic polyacrylamide curves retained their linearity under constant ionic strength (Fig's

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* Slight discrepencies between sensitivities shown here and those found in previous work (3, 5, 6) were a result of errors due to the use of different reagent and standard solutions. However, the same reagent and standard solutions were used to derive the data in Table 2 in order to make valid comparisons between sensitivities.

4 and 6).

The sensitivity of the leuco crystal violet method was slightly lower than the triiodide and starch-triiodide methods. However, the sensitivity was improved 7 to 8 fold by extraction of the developed leuco crystal violet dye from the aqueous to a methylene chloride medium (Fig. 7). It was found that 1 ml of methylene chloride was capable of efficiently extracting the colour developed by 3 ug of anionic polyacrylamide in 3 ml of aqueous solution. However, extremely high blanks became a problem when the ratio of prepared aqueous solution to methylene chloride exceeded 2.5 to 1. With a 2.5 to 1 aqueous to methylene chloride extraction, the method was linear up to 42 ug of anionic polyacrylamide and sensitive down to 0.05 ug.

Coal Wash Water Interference

Previous work showed that ferrous and ferric ion, iodide, and several organic contaminants interfered with the results of the triiodide, starch-triiodide and leuco crystal violet methods for the determination of polyacrylamide. Phenol, humic acid and maleic acid had adverse effects on all three methods. Acetone and iodide had a large, negative effect on the triiodide and starch-triiodide methods. However, acetone actually enhanced the colour development in the leuco crystal violet method and iodide had a relatively small effect. A summary of contaminant limits for the methods (Table 4) illustrated that the starch-triiodide and

TABLE 4
COMPARISON OF CONTAMINANT LIMITS FOR VARIOUS METHODS

CONTAMINANT	TOLERABLE CONCENTRATION IN A 20ml SAMPLE VOLUME (ppm)		
	TRIIODIDE METHOD	STARCH-TRIIODIDE METHOD	LEUCO CRYSTAL VIOLET METHOD
Divalent Calcium	50(a)	100(a)	100(a)
Divalent Magnesium	>500	500(a)	500(a)
Divalent Zinc	>500	100(a)	>500
Ferrous Ion	0.05(b)	1(b)	1(b)
Ferric Ion	0.05(b)	1(a)	1(a)
Trivalent Aluminium	20(a)	100(a)	50(a)
Sodium	>ppm	>ppm	>ppm
Ammonium	100(a)	50(a)	50(a)
Sulphate	>ppm	>ppm	>ppm
Chloride	250(a)	250(a)	250(a)
Phosphate	>ppm	>500	>500
Nitrate	>250	>500	>500
Iodide	0.05(b)	0.05(b)	25(b)
Phenol	1(b)	1(b)	1(b)
Acetone	100(b)	250(a)	>ppm
Maleic Acid	10(b)	>500	150(b)
Humic Acid	1(b)	5(b)	25(b)
Oil	ppm levels (b)	>ppm	>ppm

>ppm : Greater than ppm amounts of contaminant are allowable.
(a) : More than the specified amount causes a change in the absorbance greater than 10 %.
(b) : More than the specified amount causes a change in the absorbance greater than 0.010 units.

the leuco crystal violet methods were similar in most other respects concerning interferences, but the triiodide method was extremely sensitive to iron and organic contaminants.

Three samples of coal wash waters were examined for their effect on the results of the three methods. Results of contaminant analysis on the waters (Table 5) showed that contamination from the individual components in the waters were within the tolerable limits for all three methods. The absorbance of the coal waters at the starch-triiodide and leuco crystal violet method wavelengths (610 nm and 592 nm respectively) did not significantly interfere (Table 6). However, colour in the coal waters absorbed at a wavelength of 287 nm making sample blanks neccessary for polyacrylamide analysis by the triiodide method.

Coal wash water samples were prepared by filtration of suspended solids and by filtration plus methylene chloride extraction of organic contaminants as described in the Experimental section. The variously prepared samples were introduced separately to the three methods as interfering contaminants. The effects of the coal waters on the results of the three methods were studied both in the presence and absence of polyacrylamide as well as under standard and constant ionic strength conditions. Tables 7, 8 and 9 show the changes in the absorbances from the contaminant-free situation which were due to the addition of various amounts

TABLE 5
COAL WASH WATER ANALYSIS RESULTS

PARAMETER	RESULTS			LIMIT OF DETECTION
	SAMPLE 1	SAMPLE 2	SAMPLE 3	
Iron (ppm):				
Total	N.D.	79.0	552.0	2
Free	N.D.	N.D.	N.D.	0.3
Zinc (ppm):				
Total	0.8	0.9	3.0	--
Free	N.D.	N.D.	N.D.	0.2
Sodium (ppm):				
Total	35.8	104.4	65.5	--
Free	8.3	96.5	53.6	--
Calcium (ppm):				
Total	25.8	57.7	312.9	--
Free	25.8	7.1	24.7	--
Magnesium (ppm):				
Total	11.5	23.4	93.5	--
Free	11.5	5.8	8.6	--
Suspended Matter (%)	N.D.	1.8	7.2	0.1
Free Ammonium (ppm)	0.06	0.13	0.29	--
Free Chloride (ppm)	22.1	12.4	6.9	--
Free Phosphate (ppm)	N.D.	N.D.	N.D.	0.3
Phenol (ppm)	N.D.	N.D.	N.D.	0.03
Hydrocarbons, less than 12 carbon (ppm)	N.D.	N.D.	N.D.	0.5
pH	8.34	8.38	7.30	--
Conductivity (micromhos/cm)	330.0	600.0	625.0	--

N.D.= Not Detected

of coal wash water samples into the triiodide, starch-triiodide and leuco crystal violet methods, respectively.

TABLE 6

COAL WASH WATER ABSORBANCES
AT METHOD WAVELENGTHS

SAMPLE:	ABSORBANCES (Path Length = 1 cm)		
Sample # and Method of Purification	Triiodide Method Wavelength =287 nm	Starch-Triiodide Method Wavelength =610 nm	Leuco Crystal Violet Method Wavelength =592 nm
Sample 1 :			
filtered	0.013	0.003	0.006
filtered and extracted	0.007	0.002	0.000
Sample 2 :			
filtered	0.024	0.001	0.005
filtered and extracted	0.009	0.002	0.000
Sample 3 :			
filtered	0.079	0.005	0.008
filtered and extracted	0.024	0.001	0.000

The coal wash waters effected all three method results. Filtered coal wash water caused high absorbances for both the leuco crystal violet and triiodide methods when measured against a sample blank and with constant anionic PAM mass. They also developed colour with the two methods when PAM was absent. Under the same conditions, the starch-triiodide method produced erratic results, however, the coal waters generally decreased the absorbance. The decrease occurred

TABLE 7
EFFECT OF COAL WASH WATERS ON
THE TRIIODIDE METHOD

Coal Wash Water	Change in Absorbance from the Blank *				
	Filtered Coal Wash Waters			Filtered & Extracted Coal Wash Waters	
Sample Number and Volume Added	Without PAM	Constant PAM	Constant Ionic Strength	Without PAM	Constant PAM
Sample 1 :					
2 ml	not done	+0.004	+0.013	not done	-0.020
5 ml	-0.029	+0.011	+0.031	+0.002	-0.050
10 ml	-0.017	+0.048	+0.053	+0.072	-0.072
Sample 2 :					
2 ml	not done	+0.013	+0.012	not done	-0.066
5 ml	+0.017	+0.002	+0.018	+0.047	-0.088
10 ml	+0.015	+0.048	+0.056	+0.039	-0.090
Sample 3 :					
2 ml	not done	+0.003	+0.039	not done	-0.069
5 ml	+0.025	+0.061	+0.059	+0.005	-0.043
10 ml	+0.056	+0.081	+0.085	+0.065	-0.048

Experimental Conditions:					
Experiment #	MCE 36	MCE 30	MCE 31	MCE 36	MCE 36
Final Volume	37.2 ml	37.2 ml	37.2 ml	37.2 ml	37.2 ml
Dry Mass PAM	0 ug	264 ug	264 ug	0 ug	234 ug
Mass Sodium Sulphate	0 g	0 g	0.5 g	0 g	0 g
Blank Absorbance	0.068	0.991	0.730	0.068	0.975
Path Length	1 cm	1 cm	1 cm	1 cm	1 cm
Wavelength	287 nm	287 nm	287 nm	287 nm	287 nm

* Blanks were composed of distilled water samples that were treated under the triiodide method experimental conditions in the same manner as the coal water samples.

TABLE 8
EFFECT OF COAL WASH WATERS ON
THE STARCH-TRIIODIDE METHOD

Coal Wash Water / Sample Number and Volume Added	Change in Absorbance from the Blank *				
	Filtered Coal Wash Waters			Filtered & Extracted Coal Wash Waters	
	Without PAM	Constant PAM	Constant Ionic Strength	Without PAM	Constant PAM
Sample 1 :					
2 ml	not done	-0.025	-0.033	not done	-0.019
5 ml	-0.020	-0.020	-0.023	+0.026	-0.061
10 ml	-0.016	+0.001	+0.014	+0.108	-0.082
Sample 2 :					
2 ml	not done	-0.005	+0.004	not done	-0.081
5 ml	+0.044	-0.030	-0.006	+0.063	-0.125
10 ml	+0.045	-0.018	+0.017	+0.088	-0.117
Sample 3 :					
2 ml	not done	-0.037	-0.028	not done	-0.077
5 ml	-0.010	-0.008	+0.009	+0.010	-0.087
10 ml	+0.044	-0.019	+0.020	+0.055	-0.099
Experimental Conditions:					
Experiment #	MCE 34	MCE 28	MCE 29	MCE 34	MCE 34
Final Volume	46 ml	46 ml	46 ml	46 ml	46 ml
Dry Mass PAM	0 ug	273 ug	273 ug	0 ug	234 ug
Mass Sodium Sulphate	0 g	0 g	0.5 g	0 g	0 g
Blank Absorbance	0.027	0.990	0.729	0.027	0.960
Path Length	1 cm	1 cm	1 cm	1 cm	1 cm
Wavelength	610 nm	610 nm	610 nm	610 nm	610 nm

* Blanks were composed of distilled water samples that were treated under the starch-triiodide method experimental conditions in the same manner as the coal water samples.

TABLE 9
EFFECT OF COAL WASH WATERS ON
THE LEUCO CRYSTAL VIOLET METHOD

Coal Wash Water	Change in Absorbance from the Blank *				
	Filtered Coal Wash Waters			Filtered & Extracted Coal Wash Waters	
Sample Number and Volume Added	Without PAM	Constant PAM	Constant Ionic Strength	Without PAM	Constant PAM
Sample 1 :					
2 ml	not done	+0.007	-0.030	not done	+0.013
5 ml	+0.026	+0.026	+0.022	+0.024	-0.009
10 ml	+0.029	+0.030	+0.010	+0.052	-0.015
Sample 2 :					
2 ml	not done	+0.038	+0.038	not done	-0.013
5 ml	+0.047	+0.044	+0.044	+0.053	-0.016
10 ml	+0.045	+0.052	+0.054	+0.060	+0.005
Sample 3 :					
2 ml	not done	+0.050	+0.078	not done	-0.030
5 ml	+0.017	+0.054	+0.038	+0.006	+0.005
10 ml	+0.036	+0.087	+0.044	+0.074	+0.013

Experimental Conditions:					
Experiment #	MCE 35	MCE 26	MCE 27	MCE 35	MCE 35
Final Volume	50 ml	50 ml	50 ml	50 ml	50 ml
Dry Mass PAM	0 ug	273 ug	273 ug	0 ug	234 ug
Mass Sodium Sulphate	0 g	0 g	0.5 g	0 g	0 g
Blank Absorbance	0.058	0.749	0.662	0.058	0.650
Path Length	1 cm	1 cm	1 cm	1 cm	1 cm
Wavelength	592 nm	592 nm	592 nm	592 nm	592 nm

* Blanks were composed of distilled water samples that were treated under the leuco crystal violet method experimental conditions in the same manner as the coal water samples.

despite colour development caused by the coal waters which was observed in the absence of PAM. Extraction of organic contaminants from the coal wash waters with methylene chloride reversed the positive effect on the triiodide and leuco crystal violet method results and compounded the negative effect on the starch-triiodide method when constant amounts of PAM were present. However, high absorbances were still observed for all three methods when PAM was absent. Under constant ionic strength conditions the effect of the coal waters on the triiodide and leuco crystal violet methods remained unchanged, but their negative influence on the starch-triiodide method diminished.

The results showed that erroneous polyacrylamide values for all three of the methods would be obtained for a 10 ml sample of coal wash water with less than 10 ppm of PAM. Higher concentrations of PAM in coal water samples would give results within 10 % of the actual amount. All three methods were sensitive to organic contaminants which caused high results but they were removed easily by a methylene chloride extraction. The starch-triiodide method was more sensitive to negative ionic strength interferences than the triiodide and leuco crystal violet methods. However, the magnitutde of the combined effects from the coal wash waters was equivilent for all three methods.

Small amounts of suspended matter in the coal waters that

eluded the filtration process, also had an effect on the starch-triiodide and leuco crystal violet methods. The particles acted in the same manner as activated charcoal by absorbing the colour developed by polyacrylamide in the two methods. Hence, low results were observed. One mg of dried suspended matter taken from coal wash water sample number 3, consumed 0.020 absorbance units of developed colour in both the starch-triiodide and leuco crystal violet methods. Similarily, one mg of activated charcoal was capable of consuming 0.100 absorbance units of developed starch-triiodide colour and 0.040 absorbance units of crystal violet colour developed in the leuco crystal violet method. Therefore, by comparison, the suspended matter was almost as efficient as activated charcoal in extracting colour from the two methods.

Recovery of Polyacrylamide

Purification of coal wash waters was accomplished by filtration and methylene chloride extraction to remove suspended matter and organic contaminants respectively. Recovery of a known amount of polyacrylamide after purification was determined by applying the leuco crystal violet method to distilled water and coal water samples. An initial recovery study was done after filtration of spiked samples then a separate study was applied to samples that were filtered before spiking and then extracted with methylene chloride. The purification procedures are described in the Experimental section.

Table 10 summarizes the recoveries of polyacrylamide after filtration. 90 % recovery was obtained on distilled water if it was filtered without washing. Diluting the sample to twice the original volume with washings was a reasonable compromise between sufficient washings for adequate PAM recovery and small enough dilutions to maintain PAM concentration within detectable levels. Recovery of PAM on the coal waters was inversely proportional to the amount of suspended matter in the sample water (Table 5). Repeated washings did not increase the recovery in the coal water because of a thick gel that formed from the suspended matter and PAM.

TABLE 10

RECOVERY OF POLYACRYLAMIDE
AFTER FILTRATION

Sample	Recovery	Suspended Matter	Washings Final / Initial Volume / Volume
Distilled Water	90 %	0.0 %	1.00
Distilled Water	94 %	0.0 %	1.75
Sample 1	86 %	0.0 %	1.10
Sample 2	81 %	1.8 %	1.60
Sample 3	62 %	7.2 %	1.40

Methylene chloride extraction of organics in the samples did not diminish the polyacrylamide recovery to any great extent (Table 11).

TABLE 11

RECOVERY OF POLYACRYLAMIDE AFTER EXTRACTION

Sample	Recovery
Distilled water	96%
Sample 1	91%
Sample 2	98%
Sample 3	96%

Scoggins recommended a chloroform extraction of the organics for the starch-triiodide method. He observed no loss of polyacrylamide after filtration and extraction of various coal water samples.

REFERENCES
Part IV

1. Franson, Mary Ann, ed.: "Standard Methods for the Examination of Water and Wastewater," 14th edition, American Public Health Association, Washington, D.C. (1976).

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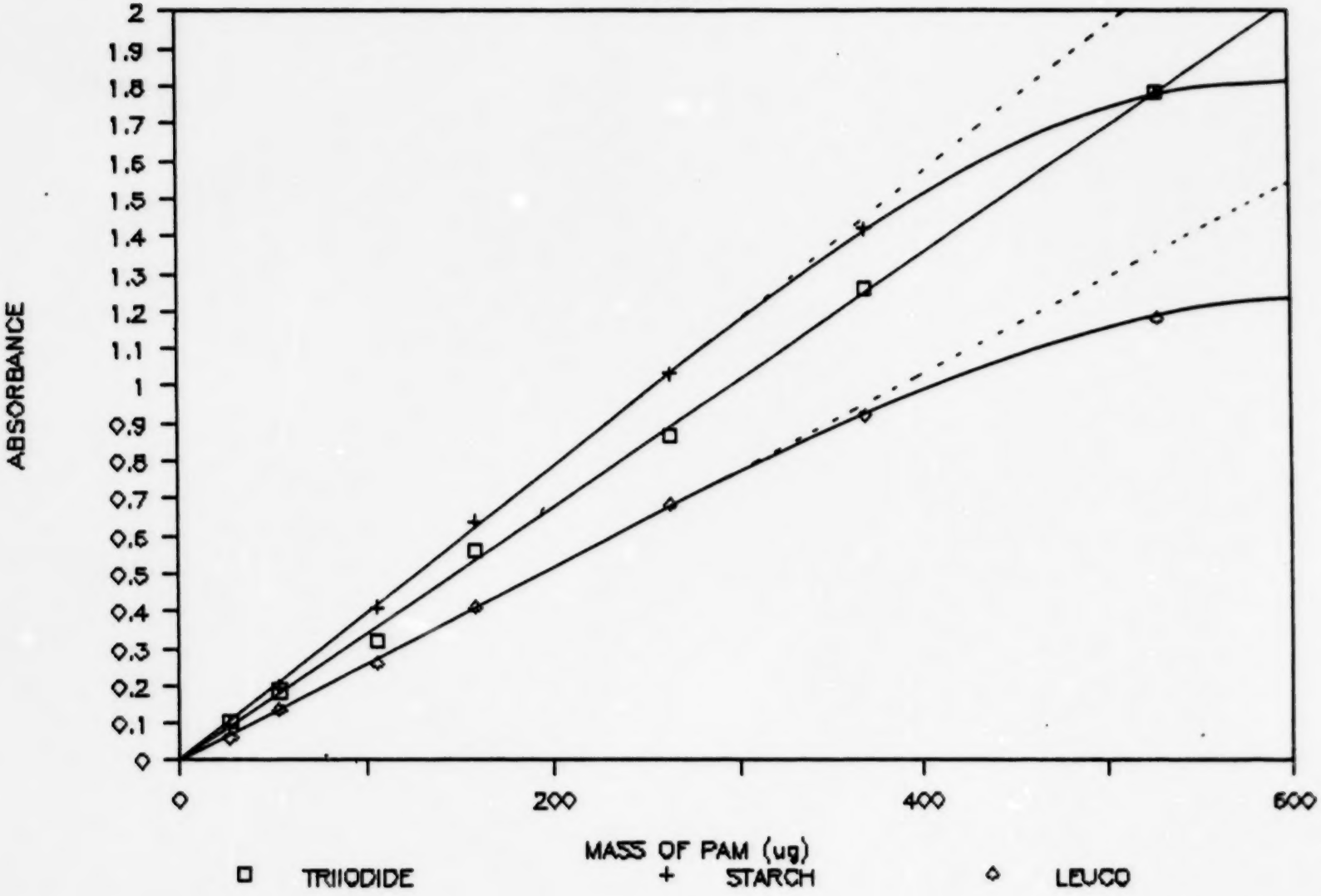
PART IV

Anionic PAM Curve
Figure 1

#	Dry Mass PAM (ug)	Absorbance - Intercept		
		Triiodide Method	Starch-Triiodide Method	Leuco Crystal Violet Method
blk	0.0	0.066	0.004	-0.058
1	26.4	0.107	0.094	0.061
2	52.7	0.185	0.196	0.136
3	105.4	0.318	0.410	0.259
4	158.1	0.559	0.639	0.411
5	263.6	0.871	1.034	0.684
6	369.0	1.259	1.419	0.923
7	527.1	1.786	1.783	1.182
Linear Statistics:				
	Points Used	1-7	1-6	1-6
	Intercept	0.131	0.006	0.096
	Cor. Coef.	0.999	1.000	0.999
	1/Slope	295.6	257.4	394.5
Experimental Conditions:				
	Experiment #	MCE 8	MCE 10	MCE 12
	Final Volume	37.2 ml	46 ml	50 ml
	Path Length	1 cm	1 cm	1 cm
	Wavelength	287 nm	610 nm	592 nm

ANIONIC PAM CURVES

FIGURE 1



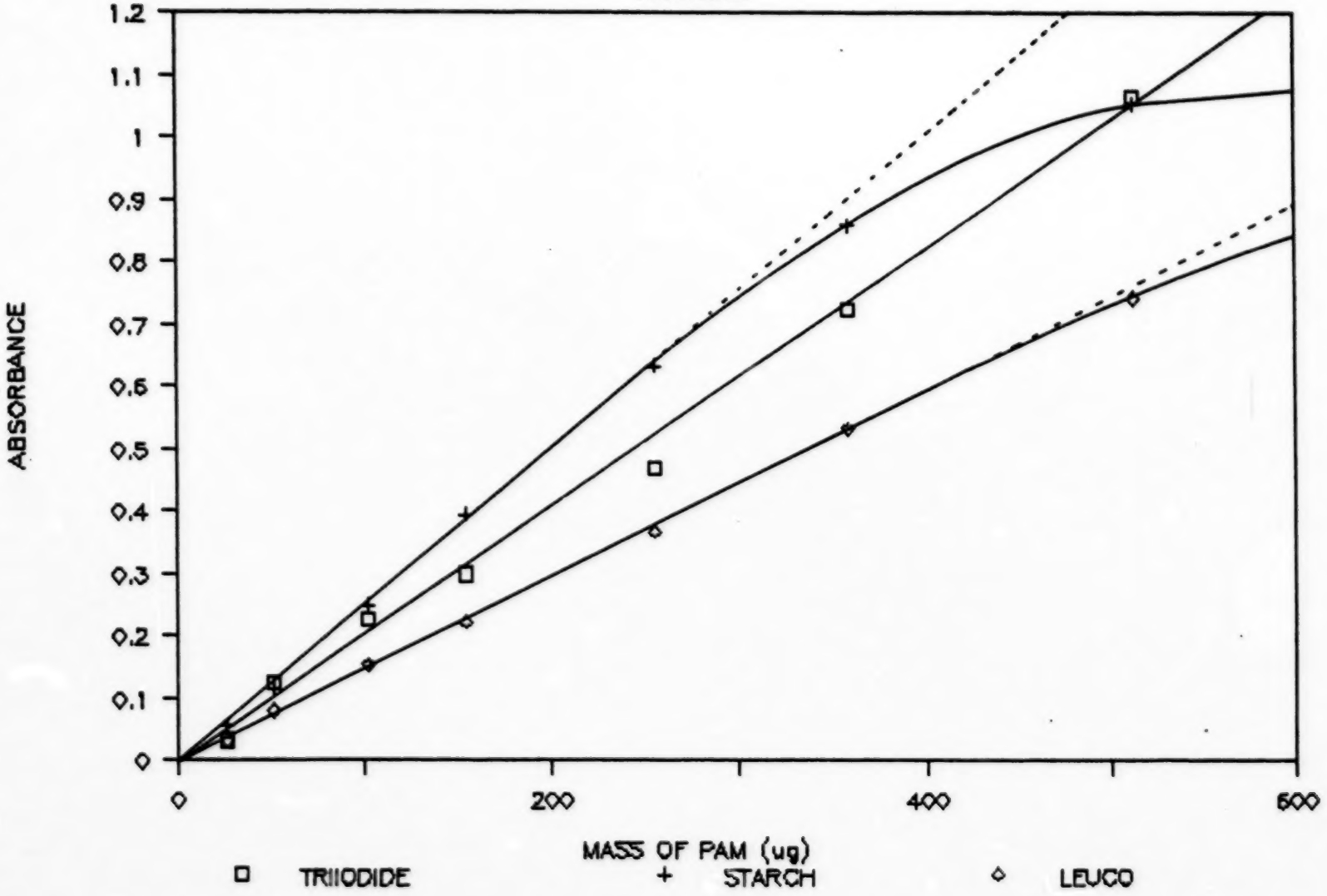
PART IV

Cationic PAM Curve
Figure 2

#	Dry Mass PAM (ug)	Absorbance - Intercept		
		Triiodide Method	Starch-Triiodide Method	Leuco Crystal Violet Method
blk	0.0	-0.182	0.014	-0.063
1	25.6	0.033	0.056	0.032
2	51.2	0.126	0.115	0.080
3	102.4	0.226	0.250	0.153
4	153.6	0.300	0.396	0.222
5	256.0	0.469	0.635	0.368
6	358.4	0.726	0.860	0.533
7	511.9	1.067	1.055	0.743
Linear Statistics:				
	Points Used	1-4,6,7	1-6	1-7
	Intercept	0.209	-0.010	0.101
	Cor. Coef.	0.999	0.999	1.000
	1/Slope	486.9	410.0	685.5
Experimental Conditions:				
	Experiment #	MCE 14	MCE 16	MCE 18
	Final Volume	37.2 ml	46 ml	50 ml
	Path Length	1 cm	1 cm	1 cm
	Wavelength	287 nm	610 nm	592 nm

CATIONIC PAM CURVES

FIGURE 2



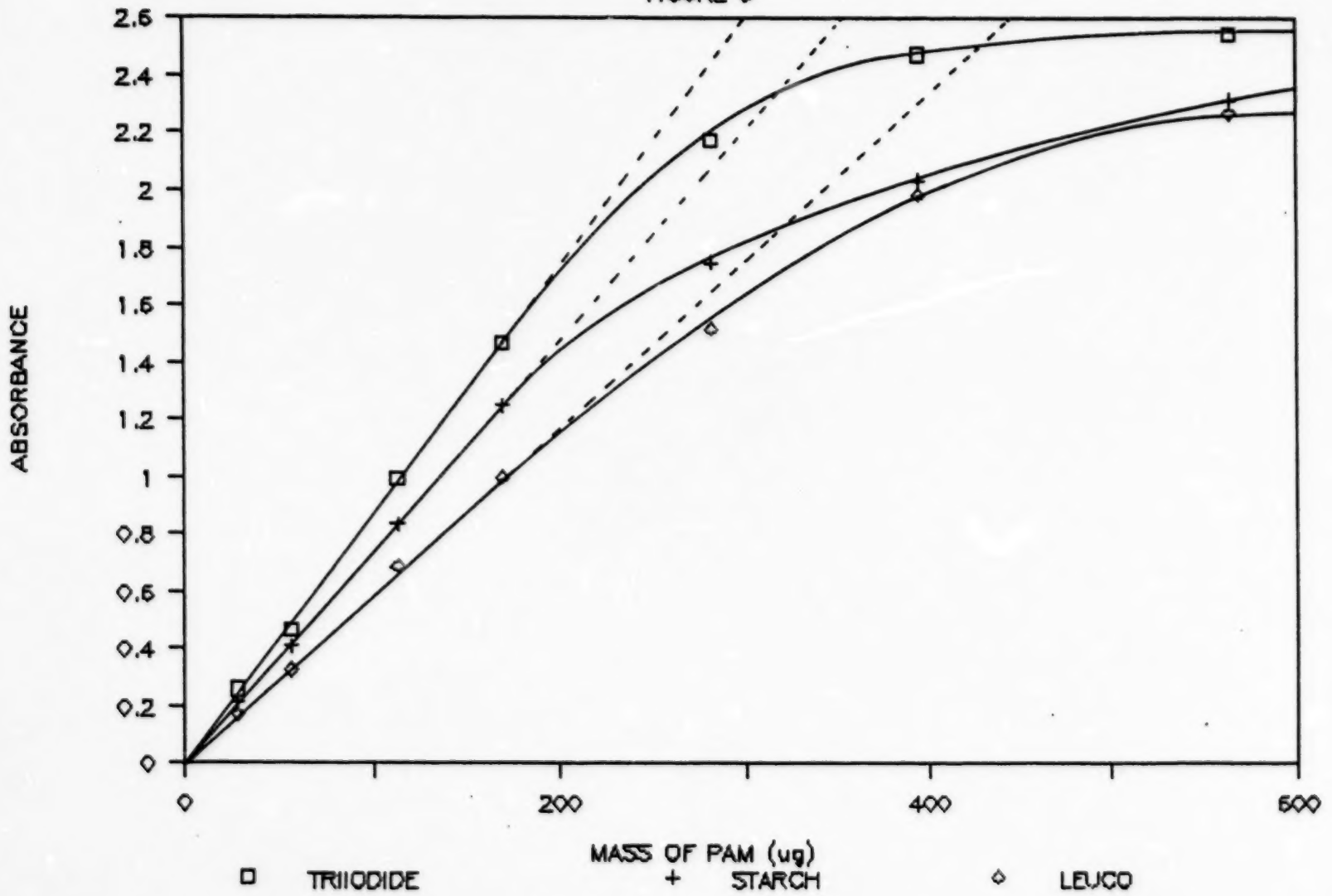
PART IV

Non-ionic PAM Curve
Figure 3

#	Dry Mass PAM (ug)	Absorbance - Intercept		
		Triiodide Method	Starch-Triiodide method	Leuco Crystal Violet Method
blk	0.0	0.008	-0.004	-0.043
1	28.2	0.259	0.213	0.169
2	56.4	0.466	0.410	0.327
3	112.8	0.995	0.834	0.685
4	169.2	1.466	1.249	1.001
5	282.0	2.178	1.747	1.517
6	394.9	2.478	2.038	1.985
7	564.1	2.548	2.316	2.272
Linear Statistics:				
	Points Used	1-4	1-4	1-4
	Intercept	0.052	0.008	0.073
	Cor. Coef.	0.999	1.000	1.000
	1/Slope	115.1	135.5	167.9
Experimental Conditions:				
	Experiment #	MCE 20	MCE 22	MCE 24
	Final Volume	37.2 ml	46 ml	50 ml
	Path Length	1 cm	1 cm	1 cm
	Wavelength	287 nm	610 nm	592 nm

NON–IONIC PAM CURVES

FIGURE 3



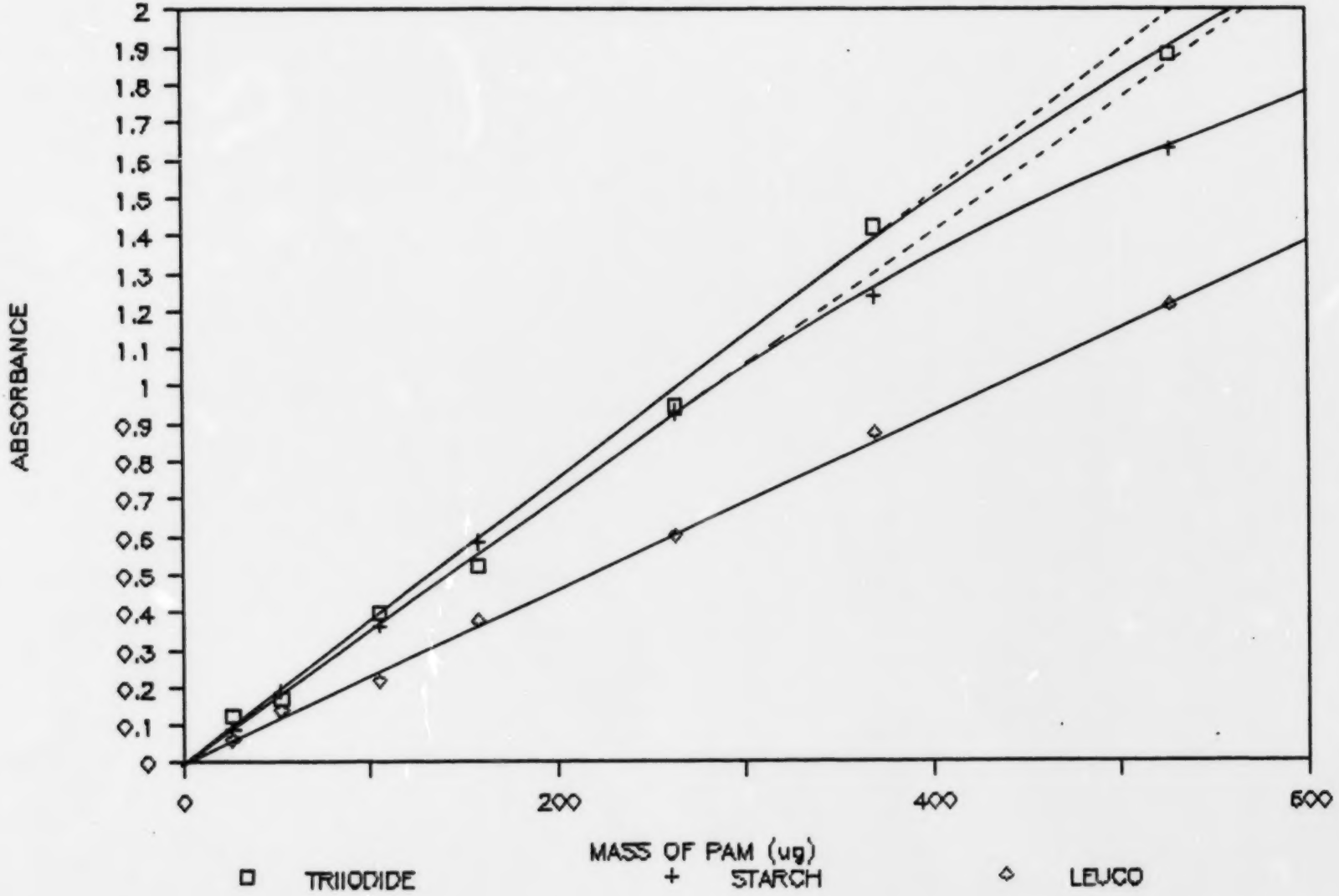
PART IV

Anionic PAM Curve
Constant Ionic Strength
Figure 4

#	Dry Mass PAM (ug)	Absorbance - Intercept		
		Triiodide Method	Starch-Triiodide Method	Leuco Crystal Violet Method
blk	0.0	0.060	-0.006	-0.039
1	26.4	0.126	0.091	0.059
2	52.7	0.168	0.189	0.139
3	105.4	0.400	0.363	0.218
4	158.1	0.524	0.584	0.379
5	263.6	0.944	0.931	0.601
6	369.0	1.421	1.236	0.875
7	527.1	1.884	1.628	1.214
Linear Statistics:				
	Points Used	1-7	1-5	1-7
	Intercept	0.104	0.014	0.059
	Cor. Coef.	0.998	0.999	0.999
	1/Slope	274.8	280.7	431.4
Experimental Conditions:				
	Experiment #	MCE 9	MCE 11	MCE 13
	Final Volume	37.2 ml	46 ml	50 ml
	Sodium Sulphate Mass	0.5 g	0.5 g	0.5 g
	Path Length	1 cm	1 cm	1 cm
	Wavelength	287 nm	610 nm	592 nm

ANIONIC PAM; CONSTANT IONIC STRENGTH

FIGURE 4



PART IV

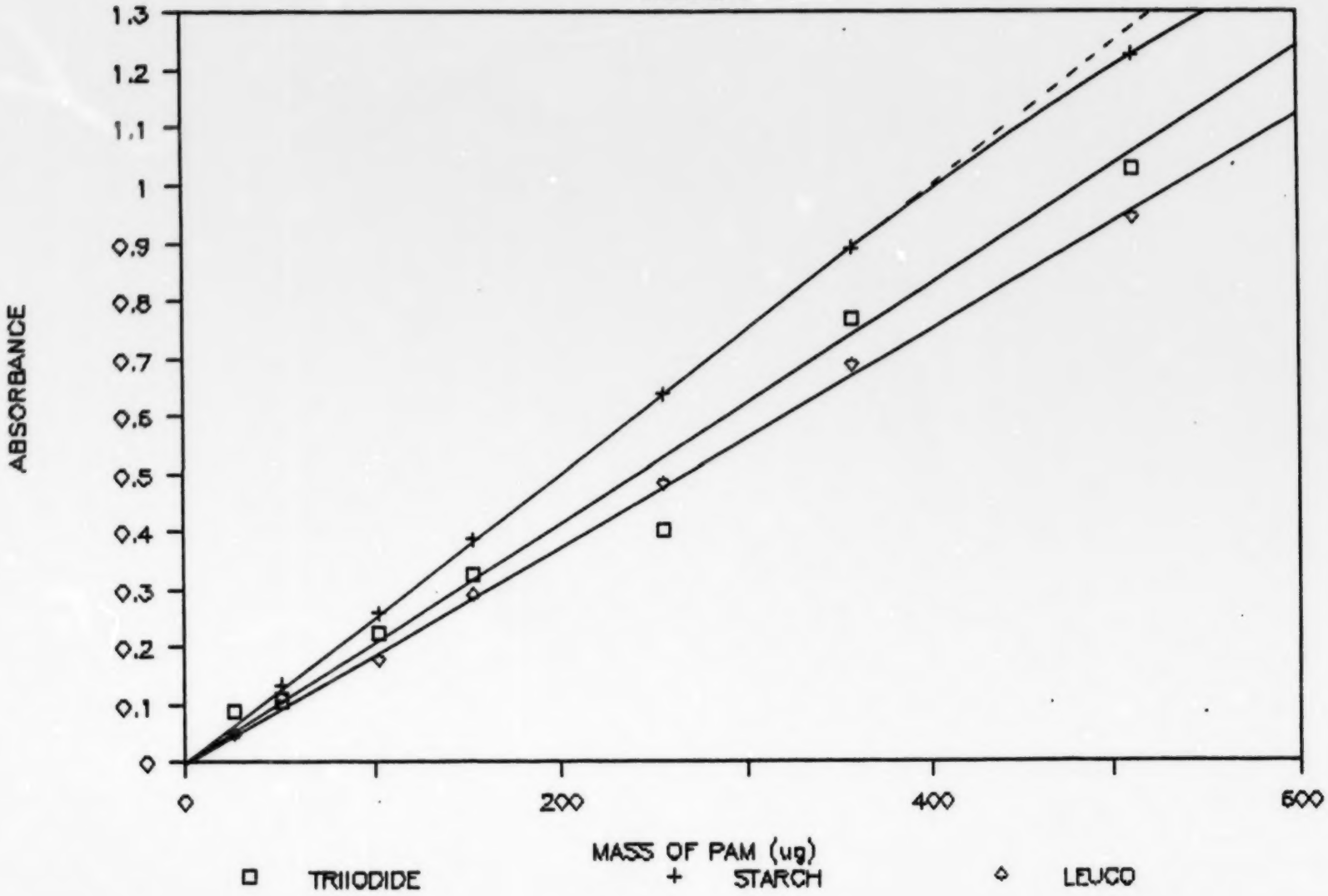
Cationic PAM Curve
Constant Ionic Strength
Figure 5

#	Dry Mass PAM (ug)	Absorbance - Intercept		
		Triiodide Method	Starch-Triiodide Method	Leuco Crystal Violet Method
blk	0.0	-0.007 *	0.001	-0.033
1	25.6	0.088	0.051	0.049
2	51.2	0.108	0.135	0.114
3	102.4	0.225	0.259	0.180
4	153.6	0.326	0.388	0.292
5	256.0	0.402	0.638	0.486
6	358.4	0.770	0.892	0.689
7	511.9	1.027	1.226	0.944
Linear Statistics:				
	Points Used	2-4,6	1-6	1-6
	Intercept	0.120	0.004	0.051
	Cor. Coef.	1.000	1.000	0.999
	1/Slope	465.6	400.4	524.5
Experimental Conditions:				
	Experiment #	MCE 15	MCE 17	MCE 19
	Final Volume	37.2 ml	46 ml	50 ml
	Sodium Sulphate Mass	0.5 g	0.5 g	0.5 g
	Path Length	1 cm	1 cm	1 cm
	Wavelength	287 nm	610 nm	592 nm

* Erratic results (absorbances taken from the avererage of two values).

CATIONIC PAM; CONSTANT IONIC STRENGTH

FIGURE 5



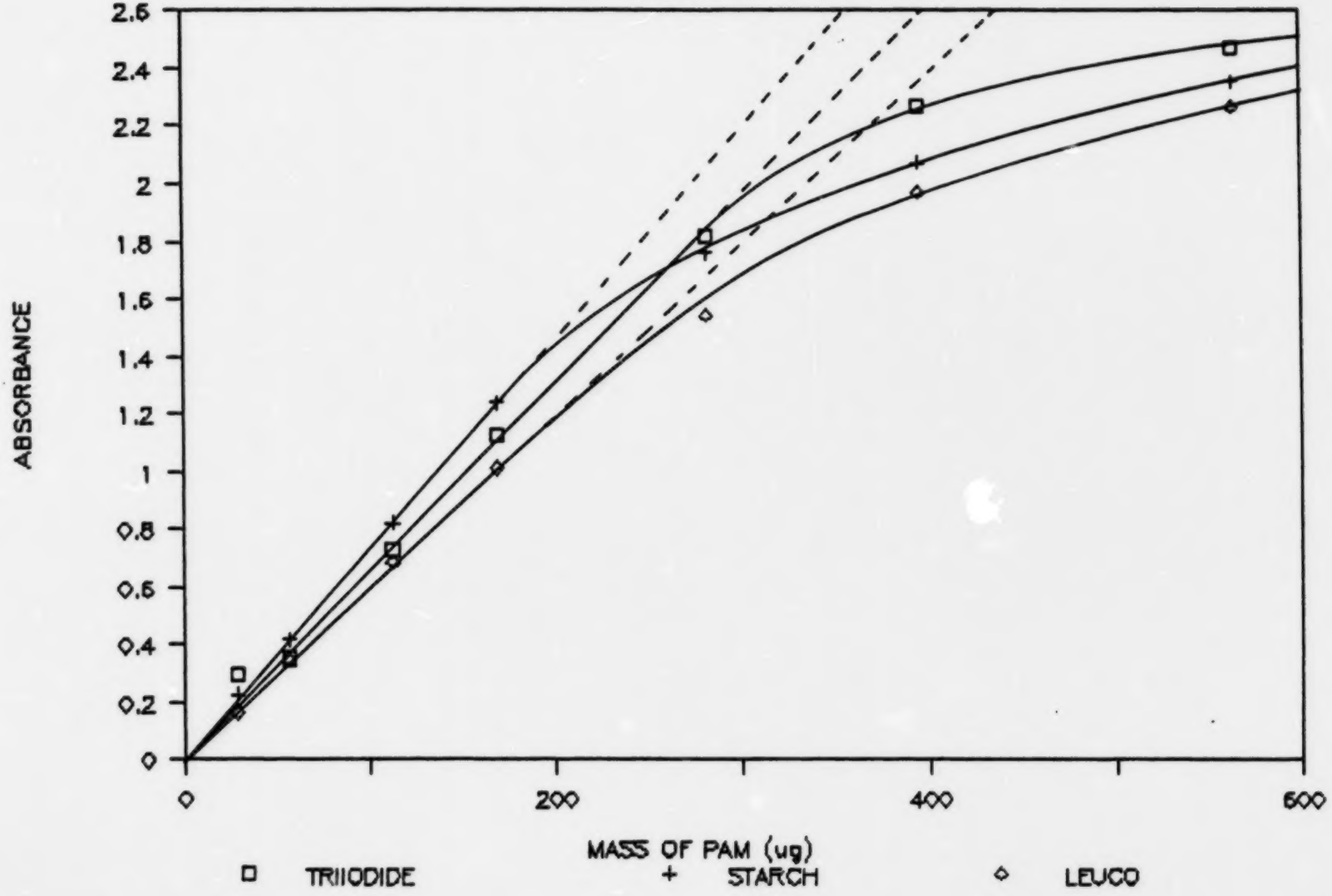
PART IV

Non-ionic PAM Curve
Constant Ionic Strength
Figure 6

#	Dry Mass PAM (ug)	Absorbance - Intercept		
		Triiodide Method	Starch-Triiodide Method	Leuco Crystal Violet Method
blk	0.0	-0.017	0.011	-0.054
1	28.2	0.298	0.228	0.165
2	56.4	0.352	0.418	0.344
3	112.8	0.732	0.822	0.685
4	169.2	1.130	1.241	1.015
5	282.0	1.815	1.759	1.545
6	394.9	2.267	2.070	1.969
7	564.1	2.471	2.354	2.266
Linear Statistics:				
	Points Used	2-5	1-4	1-4
	Intercept	0.097	0.018	0.068
	Cor. Coef.	0.999	1.000	1.000
	1/Slope	154.1	138.9	166.1
Experimental Conditions:				
	Experiment #	MCE 21	MCE 23	MCE 25
	Final Volume	37.2 ml	46 ml	50 ml
	Sodium Sulphate Mass	0.5 g	0.5 g	0.5 g
	Path Length	1 cm	1 cm	1 cm
	Wavelength	287 nm	610 nm	592 nm

NON–IONIC PAM; CONSTANT IONIC STRENGTH

FIGURE 6



PART IV

PAM Curve by the Leuco Crystal Violet Method;

With a 2.5 : 1 Aqueous to Methylene Chloride Extraction of the Developed Colour

Figure 7

#	Dry Mass PAM (ug)	Absorbance - Intercept	
		Before Extraction	After Extraction
blk	0.0	0.008	0.158
1	10.5	0.034	0.186
2	26.4	0.069	0.543
3	52.7	0.173	1.013
4	79.1	0.217	1.108
5	105.4	0.295	1.643
6	131.8	0.376	2.093
7	158.1	0.464	2.147
8	184.5	0.538	2.170
9	210.8	0.563	2.223
10	263.6	0.704	2.259

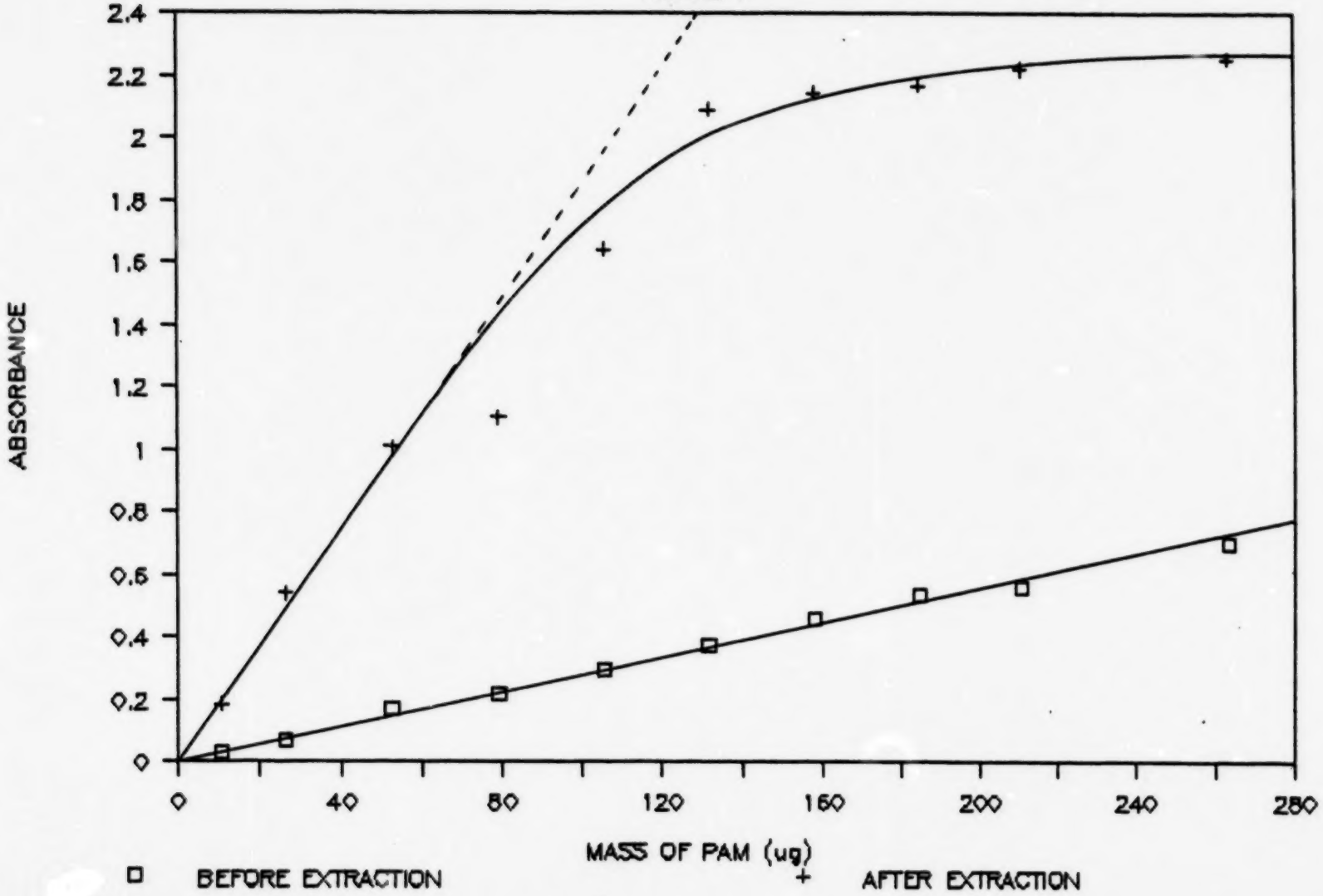
Linear Statistics:		
Points Used	1-8	1-3
Intercept	0.059	0.327
Cor. Coef.	0.998	0.998
1/Slope	345.6	51.5

Experimental Conditions:

Experiment #	MCE 33
Final Volume	50 ml
Path Length	1 cm
Wavelength	592 nm
Polyacrylamide Type	anionic

PAM CURVE; WITH CH2CI2 EXTRACTION

FIGURE 7



APPENDIX

APPENDIX 1

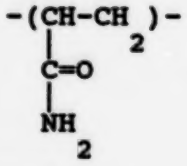
DETERMINATION OF PERCENTAGE OF ACRYLAMIDE GROUPS IN POLYACRYLAMIDES

Determination of the percent of acrylamide groups in a polyacrylamide sample was based on the alkaline hydrolysis of the amide groups (1) :

$$RCONH_2 + H_2O \xrightarrow{OH^-} RCOO^- + NH_3$$

The percent of acrylamide groups was calculated from the amount of acid required to back titrate the excess base. The method and conditions for hydrolysis were suggested by Tiwari and Sharma (Ap-2).

One unit of acrylamide on the polymer was assumed to have a molecular weight of 71 with the structure:



Also, one mole of acrylamide was hydrolysed by one mole of sodium hydroxide, hence,

Mass of Acrylamide Groups (g) = 71 (moles of reacted NaOH)

(Equation #1)

The moles of reacted NaOH was deduced by back titration of excess NaOH with hydrochloric acid. Subsequently,

$$\text{Mass of Acrylamide Groups (g)} = 71\ (\text{initial moles of NaOH} - \text{moles of HCl titrant})$$

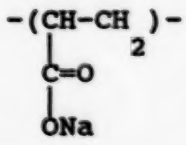
(Equation #2)

The percentage of acrylamide groups per unit mass of polymer was easily determined using Equation #2 and the known initial mass of polyacrylamide, hence,

$$\% \text{ Acrylamide Groups} = \frac{(\text{Mass of Acrylamide Groups (g)})}{(\text{Mass of Polyacrylamide (g)})}(100)$$

(Equation #3)

Calculation of the percent of acrylamide groups per unit mass of polymer was also deduced from the given percentage of amide groups replaced by carboxylate groups. This was accomplished by assuming that the hydrolysed acrylamide unit had a molecular weight of 94 with the structure:



Hence, if "x" molar percent of the amide groups were replaced by carboxylate groups, in one mole of polymer units, then,

$$\text{Total Mass of Hydrolysed Acrylamide Groups (g)} = 94\ (x/100)$$

(Equation #4)

Likewise, given the molecular weight of an acrylamide unit, then,

$$\text{Total Mass of Acrylamide Groups (g)} = 71\,(100-x)/100$$

(Equation #5)

Assuming that the polyacrylamide structure consisted of only hydrolysed and unhydrolysed acrylamide units, then,

$$\text{Total Mass of the PAM Sample (g)} = 94\,(x/100) + 71\,(100-x)/100$$

(Equation #6)

Hence,

$$\text{Percent of Acrylamide Groups per Unit Mass of Polyacrylamide} = \frac{71\,(100-x)}{94x + 71(100-x)}\,(100)$$

(Equation #7)

Equation #7 was used to convert Scoggins' results (Ap-3) for degree of hydrolysis for various polyacrylamide samples, into percent by weight of unhydrolysed acrylamide groups. The assumption made in order to derive Equation #6, restricted the application of Equation #7 to anionic and non-ionic samples of polyacrylamide.

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Ap-1 Morrison, R. R.; Boyd, R.N.: "Organic Chemistry," 3rd edition, Alyn and Bacon Inc., Toronto, Ontario (1981) page 671.

Ap-2 Tiwari, R. D.; Sharma, J. P.: "The Determination of Carboxylic Functional Groups," Pergamon Press Ltd., Toronto, Ontario (1970) pages 105 to 107.

Ap-3 Scoggins, M.W.; Miller, J.W.: "Determination of Water-Soluble Polymers Containing Primary Amide Groups Using the Starch-Triiodide Method," Society of Petroleum Engineers Journal (June, 1979) page 151.